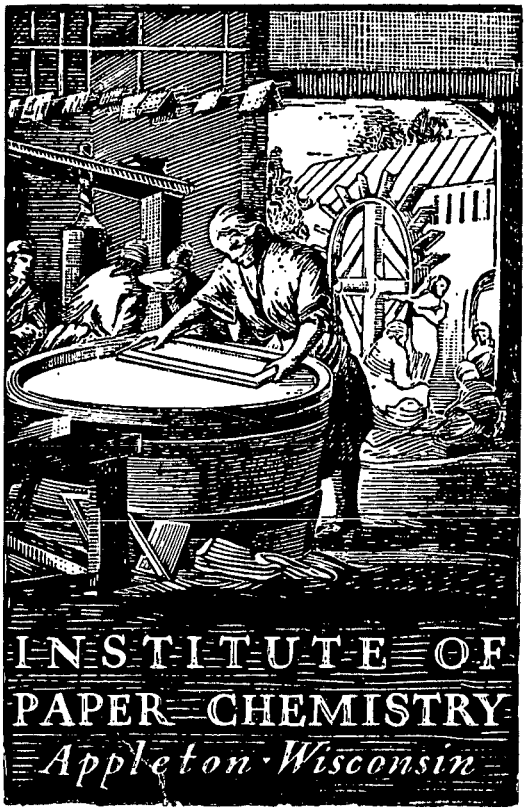

AMINE SOLVENT PULPING

Project 3354-1

Report One
A Progress Report
to
MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

August 21, 1978

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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INTRODUCTION

Project 3354-1 was initiated by Larry M. Julien during his sabbatical leave from Michigan Technological University. The work was carried out in the Chemical Sciences Division of The Institute of Paper Chemistry under the supervision of Earl W. Malcolm. The advice and counsel of John Peckham was especially valuable and is hereby acknowledged. This report constitutes a summary of the work completed.

The author and his collaborator, Dr. B. C. H. Sun from Michigan Technological University, have worked for several years pulping with a system composed of ethylenediamine (EDA) and sodium hydroxide (NaOH) water solutions. It was felt that more attention should be given to the possibility of pulping with a different amine and in the absence of NaOH. Table I shows a list of possible candidates, along with their relative base strengths and boiling temperatures. Since EDA and ethanolamine were found to be stronger pulping agents than ammonia, it was decided to proceed on the assumption that the relative basicity was related to pulping ability and to use 1,6-diamino hexane (HMDA), the strongest base. This assumption is also supported by results with mono-, di-, and triethanolamines reported by A. F. A. Wallis at 30th Appita Conference in Queenstown, N.Z. in 1976.

In addition to being a strong base, the high boiling point of HMDA offered an opportunity to pulp under atmospheric pressure. This allowed observation of pulping reactions in glass vessels and construction of experimental digesters without the necessity of machining equipment to fine tolerances in order to withstand the high pressure conditions normally encountered in pulping systems. All of the following pulping data were obtained using a combination of glass, Teflon, and stainless steel apparatus.

TABLE I

PROPERTIES OF SOME SELECTED AMINES

Compound	pKa	Boiling Point, °C
Ammonia	9.25	33
Ethanol amine	9.50	170
Methyl amine	10.66	6
Ethyl amine	10.81	17
Propyl amine	10.71	49
Butyl amine	10.77	78
1,2-Diamino ethane	10.71 7.56	117
1,3-Diamino propane	10.94 9.03	136
1,4-Diamino butane	11.15 9.71	159
1,6-Diamino hexane	11.86 10.76	204

The goals of this study were outlined in September of 1977 and are as follows:

I. Define Pulp Properties for Aspen and Southern Pine

   A. Unbleached

   B. Bleached

II. Define Handsheet-Fiber Property Relationship

   A. Define Fiber Properties

   B. Relate Fiber Properties to Handsheet Properties

III. Determine Pulping Parameters

A. Effect on Pulp Properties

B. Effect on Economic Factors

The experimental program designed to address these goals is listed next.

(a) Design and build a digester to make adequate pulp samples.

(b) Evaluate physical properties of handsheets from pulps with kappa numbers between 60 and 10 for aspen and southern pine.

(c) Bleach and repeat (b)

(d) Do chemical analyses of pulps for lignin, carbohydrate, and extractive contents.

(e) Do a crystallinity study using x-ray and Raman spectroscopy.

(f) Measure the viscosity of the pulps.

(g) Test the effect of washing with water, amine solutions, and NaOH solutions on yield, kappa numbers, and nitrogen contents of the pulps.

(h) Determine the yield, kappa number, and zero-span dependence on cooking time at 200°C.

(i) Measure the amount of amine in the black liquor solids.

This program was carried out and the following sections contain the experimental results and discussion thereof.

DIGESTER DEVELOPMENT

This section of the report contains the experimental results related to the construction and design of the digesters. It describes the evolution of a process to obtain fibers free of lignin while retaining the majority of the hemicellulose material in the fiber.

The development of digesters led to the following designs:

1. distillation column (see Fig. 1).
2. vapor boiler (see Fig. 2)
3. stirred reactor (see Fig. 3).
4. continuous atmospheric pressure reactor (see Fig. 4).

The operation of and the results obtained from these digesters are discussed in the following paragraphs.

DISTILLATION COLUMN DIGESTER

The distillation column digester was operated by bringing the system to equilibrium at a temperature of 200°C at the condenser head, turning off the boiling pot, removing the condenser, placing the chips in the column, replacing the condenser and turning the heat back on. About 50 grams of oven-dried chips were usually brought to temperature (200°C) in about 15 minutes in this manner. At the end of a specified time period, the heat was turned off, the condenser removed, the column was lifted from the boiling pot and the chips dumped into a beaker partly filled with water. The chips were then fiberized in a British disintegrator, washed, and screened for further testing.

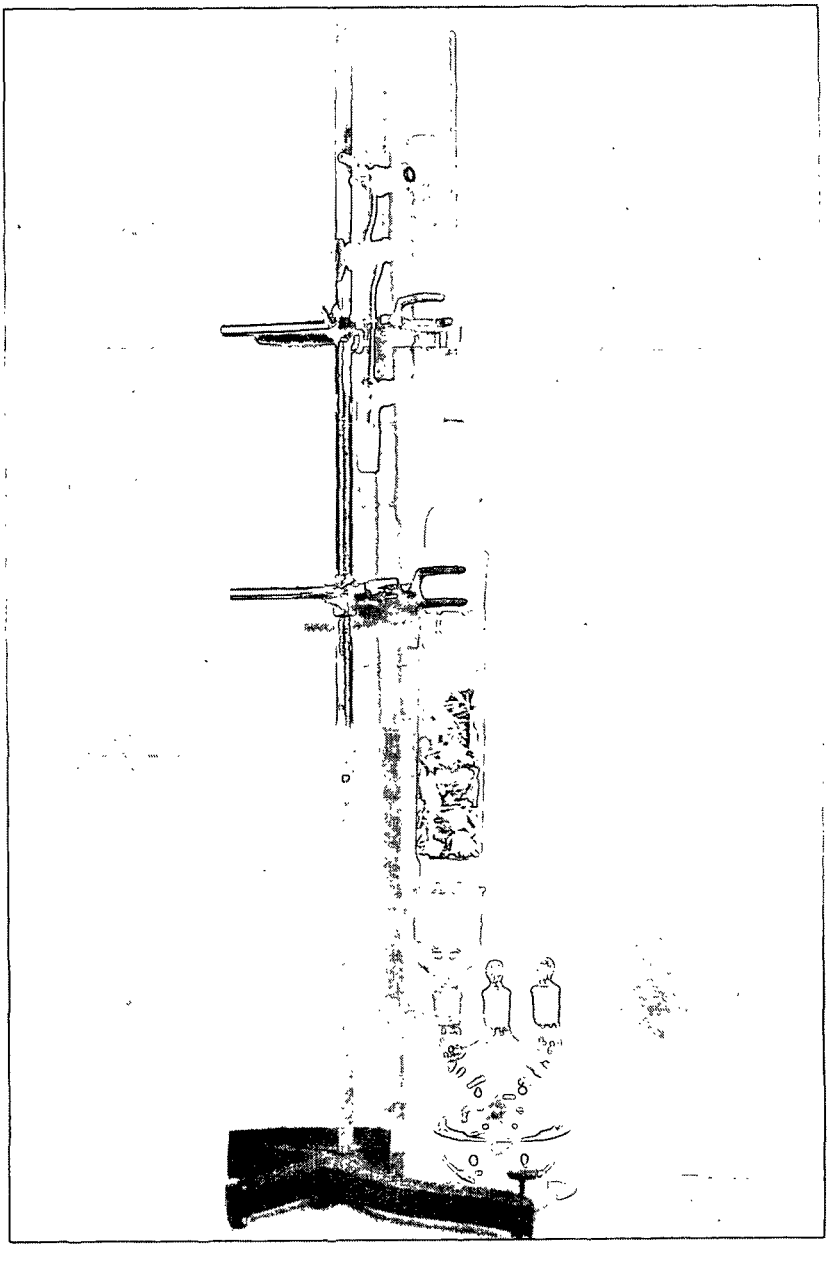

Figure 1. Distillation Column Digester

The pulp obtained in this way was used to characterize pulping parameters and the chemical properties even though these samples were generally too small for beating and bleaching purposes. This method provides a good way to characterize pulp properties and is instructive in that it is possible to watch the action of the condensing vapors on the chips in the columns during the delignification

period. The difference between spring and summer woods was particularly interesting and manifested itself by layers of dark and light regions of the chip. Further topochemical work aimed at examining the reasons for this difference in color could lead to a better understanding of liquor penetration, delignification processes and the color formation that is ultimately the target of pulping and bleaching processes.

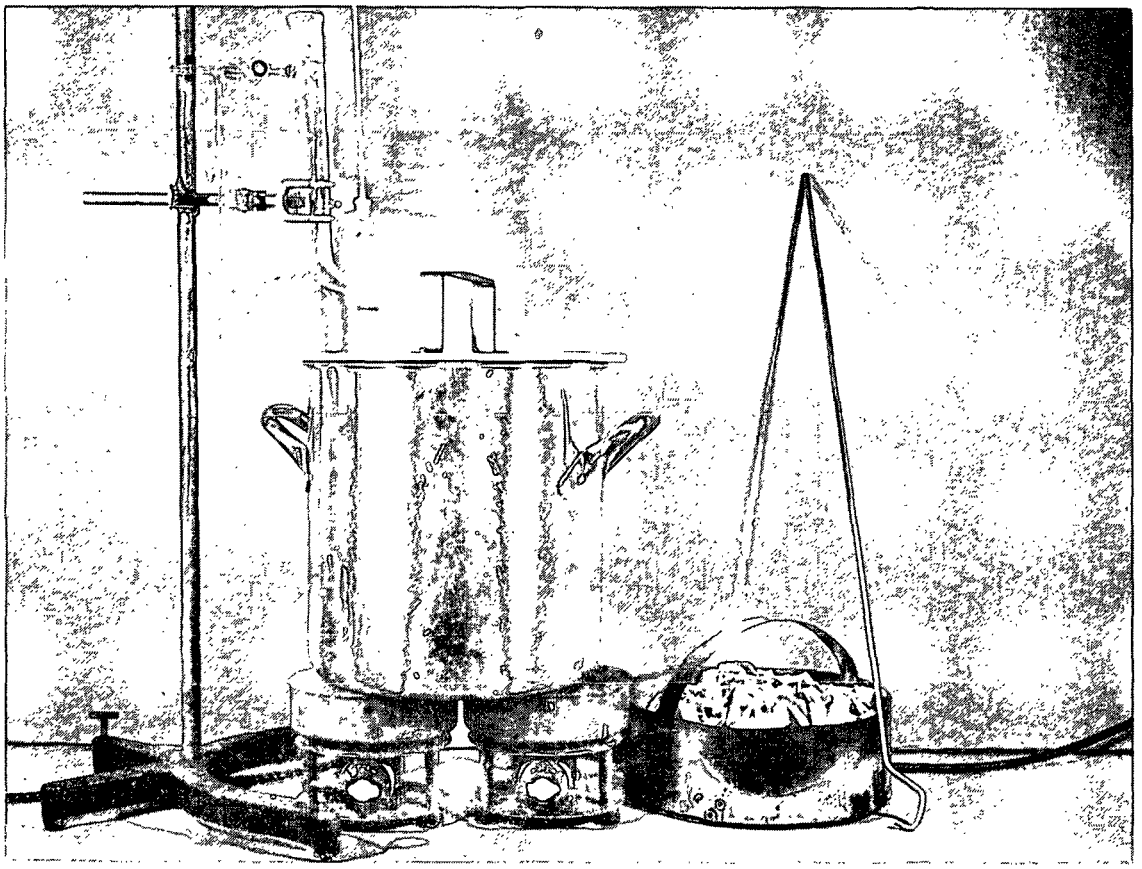

Figure 2. Vapor Boiler Digester

VAPOR BOILER DIGESTER

The vapor boiler digester shown in Fig. 2 was constructed in order to obtain large enough samples for beating and bleaching purposes. This digester was operated by placing 5 to 6 liters of HMDA liquid into the pot, putting between

500 and 600 grams (o.d. basis) of wood chips in the perforated basket, placing the basket on a stand, replacing the cover and turning on the heaters and cooking the chips in the condensed vapors. The times to and at temperature were generally longer than in the distillation column digester described earlier. The extracted chips were dumped from the basket into water and stirred to fiberize. Pulps obtained in this way were used for the beating and bleaching tests discussed later in the report.

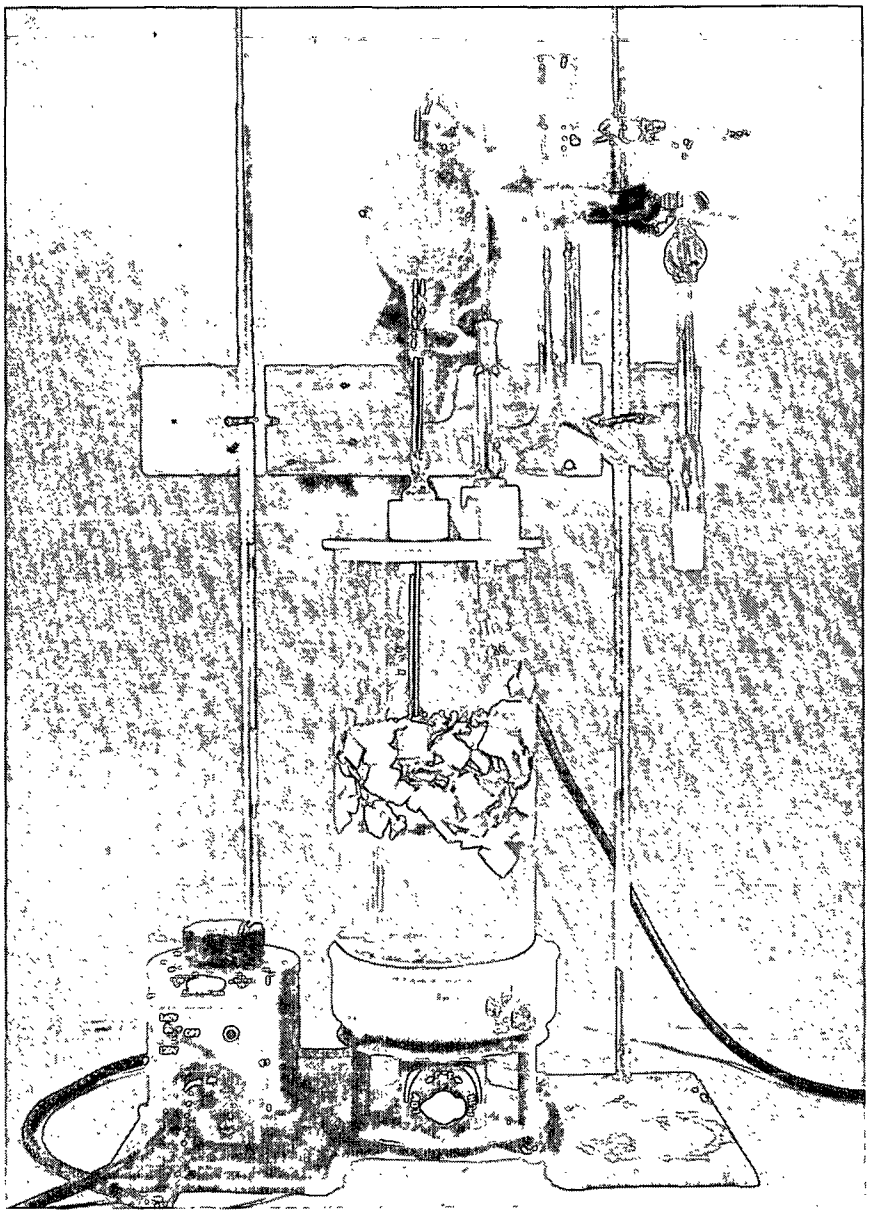

Figure 3. Stirred Reactor

The yields obtained with this digester were virtually identical to those obtained for the distillation column digester for the respective pulp species under conditions of no screened rejects. However, the kappa numbers were slightly higher. The most probable reason for this difference was the relative amount of the refluxing vapor. The distillation column digester had more vapors condensing and refluxing in the column, thus providing for a better removal of the soluble lignin that diffused out of chips. Consequently, the lignin content was lower in the chips cooked in the distillation column digester.

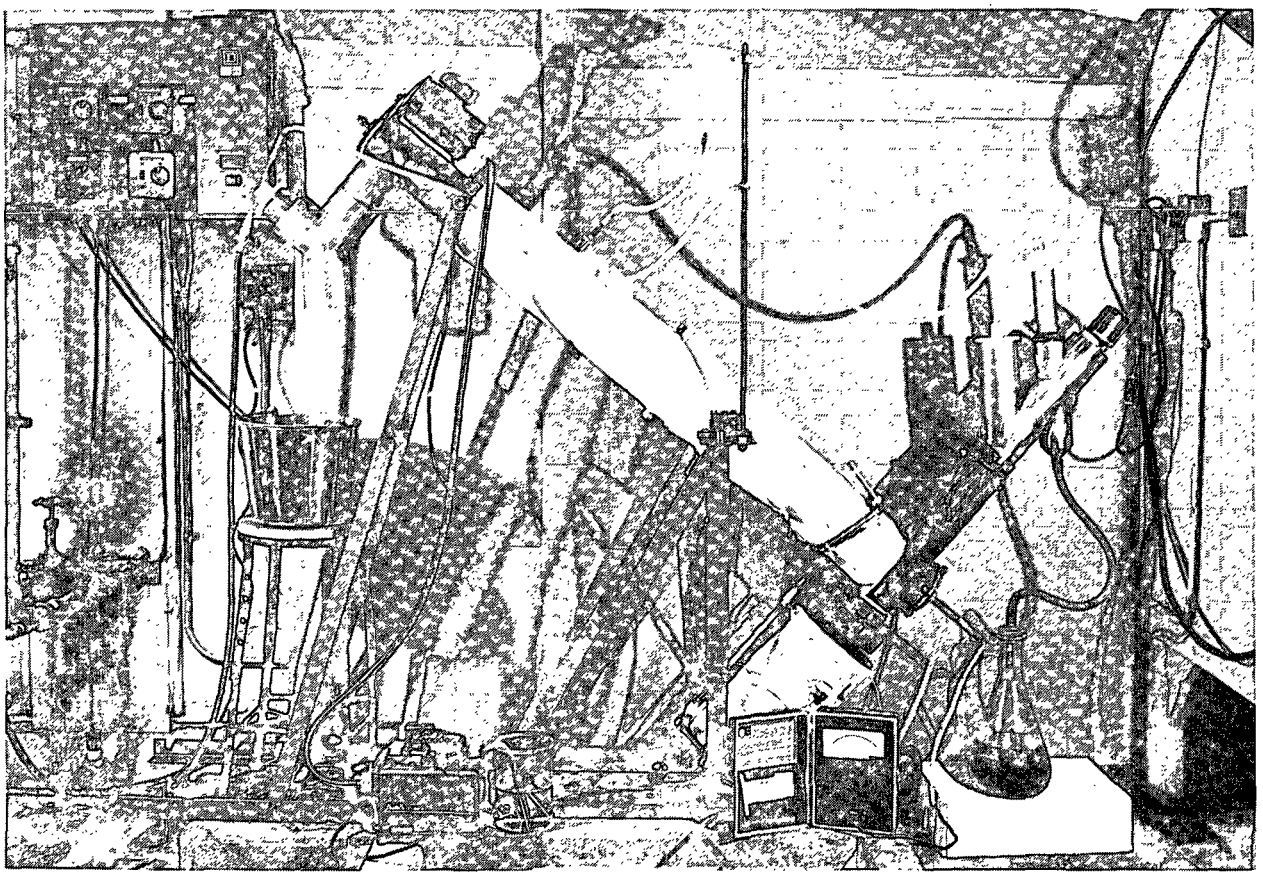

Figure 4. Continuous Atmospheric Pressure Digester

These results suggested proceeding on the basis that diffusion from the fiber through the chip is rate determining for lignin removal. Therefore, the next logical step was to decrease the size of the chip to permit faster diffusion from the fibers. This can be done by either using smaller chips or stirring the chips during the pulping reaction, causing the fibers to become separated from the chips as soon as they have lost enough lignin to become free, thus exposing the fibers to faster lignin removal. It was felt that the use of smaller chips in the distillation column or the vapor boiler would not facilitate lignin removal as well as stirring because diffusion from the fiber through the chip into the liquor would still be limiting. This concept led to the construction of the stirred reactor shown in Fig. 3.

STIRRED REACTOR DIGESTER

The stirred reactor was operated by placing 3 liters of HMDA liquid in the pot, adding 30 grams (o.d. basis) wood chips, to give a pulp suspension of approximately one percent, putting the top on, turning on the heat to bring up to temperature and stirring. Several experiments were carried out in this manner. It was noted that the chips started to break up in about one-half hour for both aspen and loblolly. However, the loblolly chips still took longer than aspen to fiberize completely, i.e., 1/2 hour for aspen and 2 hours for loblolly.

The pulps obtained from this digester were not quantitatively examined for yield, since it was difficult to separate the isolated fibers from the black liquor; i.e., pouring 2 or 3 liters of hot HMDA through a stainless steel filter was too hazardous from a safety standpoint. However, pulps with permanganate numbers as low as 6.6 were obtained from the digester.

Even this low lignin content was undoubtedly higher than the limiting value because the fibers were immersed in the black liquor during the delignification process. It's felt that contact with fresh liquor would lead to the ultimate removal of lignin somewhere below 1.0%, i.e., a permanganate number below 5.

CONTINUOUS ATMOSPHERIC DIGESTER

The other digester designed and constructed, the continuous atmospheric pressure digester, was built in order to obtain larger samples of pulp (the instantaneous capacity is between 1 and 2 kilograms of wood chips), and to test the concept of a "distillation column" digester with a moving packing consisting of wood chips. The concept consists of the following steps:

1) Wood chips are placed in the input port of the digester. They are conveyed toward the reactor tube by a combination of gravity feed and a spiral agitator. As they approach the tube, vapors from the boiler pot heat the chips and drive off the moisture. This moisture travels upward in the input port and is condensed and removed. This step of the digestion then consists of replacing the water in the chips at ambient temperatures with hot amine at 200°C.

2) The amine saturated chips at 200°C are now conveyed through the reactor tube with an auger. As they move through this region, amine vapors supplied from the boiler pot are being refluxed in a manner analogous to the liquid-vapor equilibrium that is established in a normal distillation column. This step, then, is an extraction stage for the lignin removal. It is felt that if the chips were fiberized at this point, optimum lignin removal would be obtained. Unfortunately we had no way of controlling the fiberization in the tube.

3) The last step of this concept is to inject water into the reactor tube near the exit port. With the proper control of mass and energy balances a steady state should be reached where the water displaces the amine and in doing so cools the pulp from 200°C to 100°C. This step keeps the amine confined to the reactor tube of the digester.

The net effect of the whole process is to move chips through a zone of refluxing amine vapors that removes lignin from the wood and contains the amine between two zones of water under steady state conditions. The important factors found for its operation are as follows.

First, a bent stainless steel coil that slowly rotates in the chip input port was added to the original design so that the chips did not bind as they were fed into the auger of the main body of the digester. Second, the orifices between the boiling pot and the digester tube need to be sufficiently large to allow for the return of the condensed vapors and yet not so large as to allow chips to fall through. Flooding of the column will occur if this condition is not met, making it difficult to contain the vapors inside the digester. Third, the best way to contain these vapors in the digester was to place condensers at each end of the digester.

If the pulped chip column was sufficiently long, it could act as the condenser, since a temperature drop from 200 to 150°C was found over the 2-foot length in the water input port section. The input of the chip column also acted as a condenser unless the liquid flow return to the pot was not sufficient to prevent flooding, in which case the excess vapors escaped from the input port of the digester into the hood.

These results lead to the concept that the optimal pulping process in terms of lignin removal for this system consists of separating fibers from the wood chips as soon as a gentle mechanical action will allow (i.e., fiberizing in a stirred reactor or the moving bed of a continuous digester), and then subjecting the fibers to fresh HMDA using a vapor-liquid condensation process or a countercurrent flow of fresh HMDA liquid. The purpose of this process is to liberate the fibers from the wood chips and remove as much of the lignin as possible without contaminating the fiber with the material dissolved in the pulping liquor, either in the pulping or subsequent washing stages.

STEADY STATE CONTINUOUS STIRRED REACTOR

The final step in the evolution of the digesters should be to construct a digester to examine the above concept. A schematic illustration is shown in Fig. 5 of a system that should accomplish this goal. This system is simply a stirred reactor with a screen to prevent fibers from leaving the reactor through the exit port. It can be used to continuously provide a fresh liquor so that the optimum lignin removal can be obtained. In addition, proper recirculation of the black liquor could be used to simulate a section of a continuous countercurrent reactor.

Completion and operation of this system should allow us to obtain pulp under optimum conditions in order to obtain a nearly lignin free pulp and is an important consideration for future work. Either this system or the continuous distillation column should accomplish the desired goals. However operational procedures for the continuous distillation column will probably be more difficult to develop even though it has the advantage that the whole process can be done in one unit operation. The bleaching results in the chemical treatment and analysis section (next) will lend support for this development.

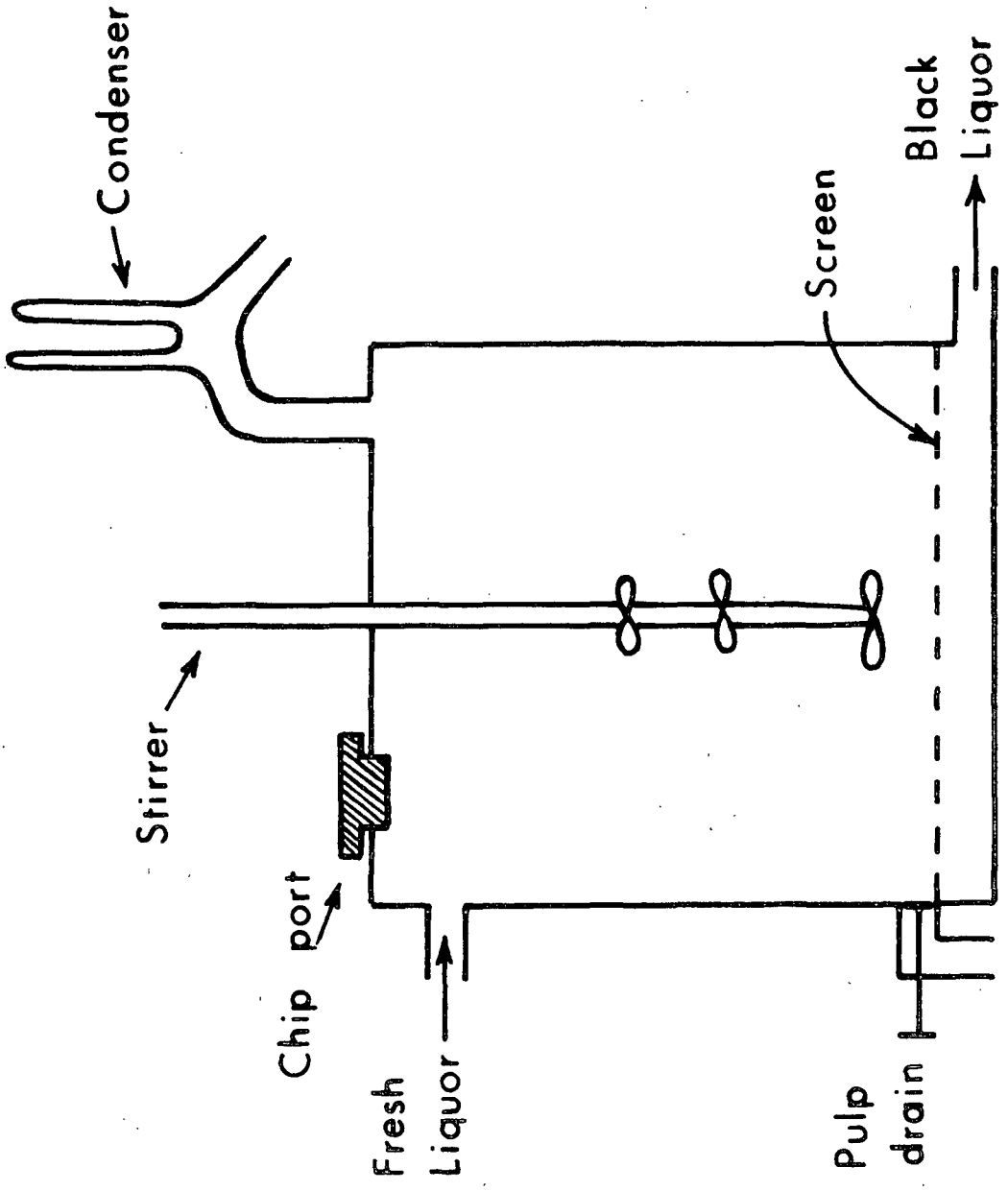

Figure 5. Schematic of a Continuous Stirred Reactor

PULP PROPERTIES

This section describes the properties of pulps obtained from treating aspen and loblolly wood chips with HMDA and representative pulps with bleaching chemicals.

AMINE TREATMENT RESULTS

The first significant fact encountered is that high yields are obtainable by pulping wood chips with HMDA both in the vapor-condensate treatment and in the liquid solution treatment. Figures 6 and 7 show plots of yield and kappa number versus time obtained for the distillation column digester with aspen and loblolly pine chips.

Note that the screened yield for aspen is approximately constant between 67 and 68% over quite a long period of cooking time and shows no sign of decreasing significantly at longer times. All of the pulps obtained in the other digesters exhibited this phenomenom, i.e., a screened yield of approximately 67% even though the kappa numbers varied between 50 and 10 and the cooking times were different. Keep in mind that there is error of about one percent in most of the yield determinations and this can account for the varying kappa numbers having the same apparent yield of 67%, assuming that the yield is really slightly different at the different kappa numbers.

The varying kappa numbers are likely due to the effectiveness of lignin removal in the pulping, fiberization and subsequent pulp washing processes. The factors that cause these differences are undoubtedly related to the solubility of the lignin in the washing solutions and the fluidity of the lignin as a function of temperature.

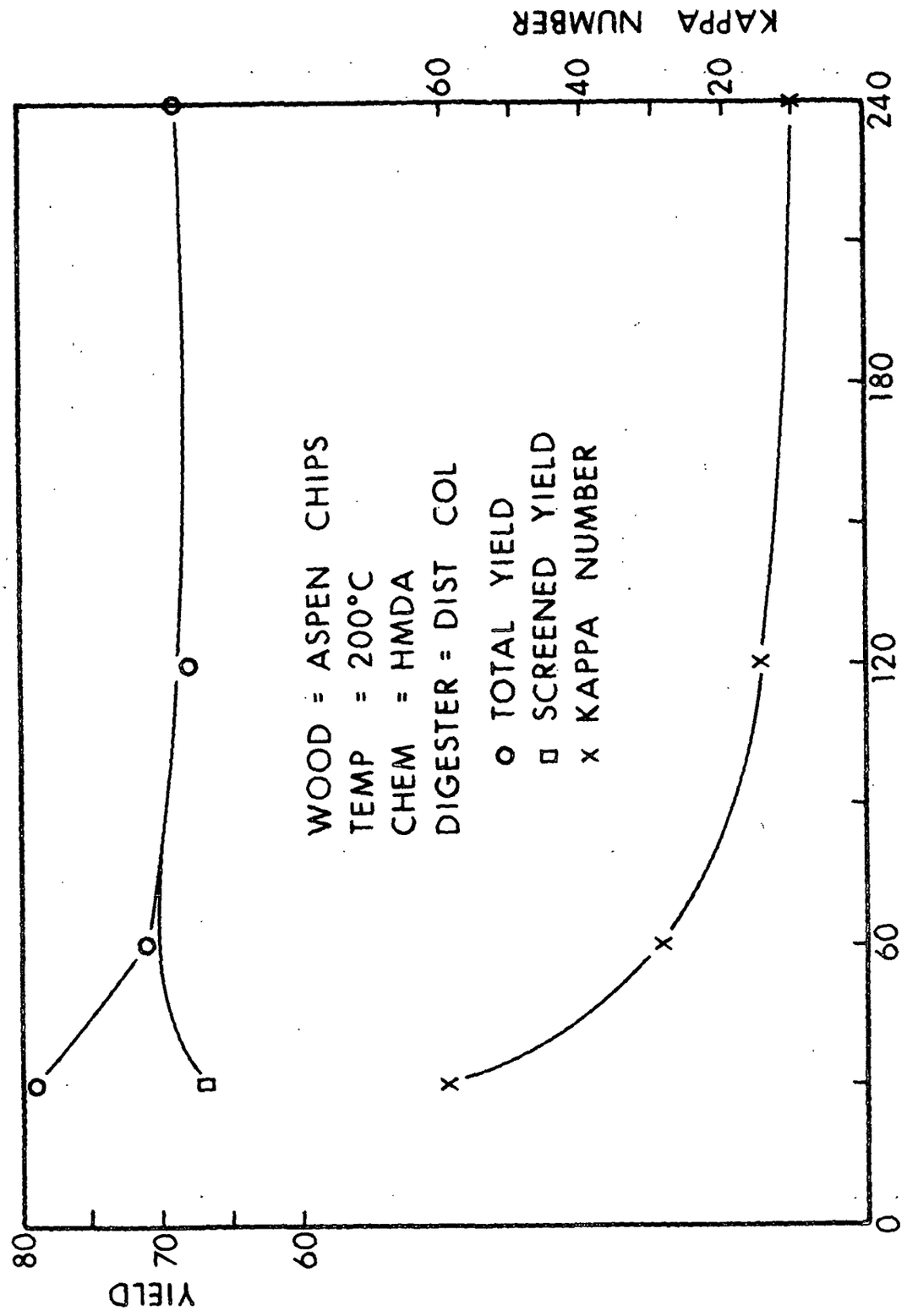

Figure 6. Yield and Kappa Number as a Function of Cooking Time for Aspen in the Distillation Column Digester

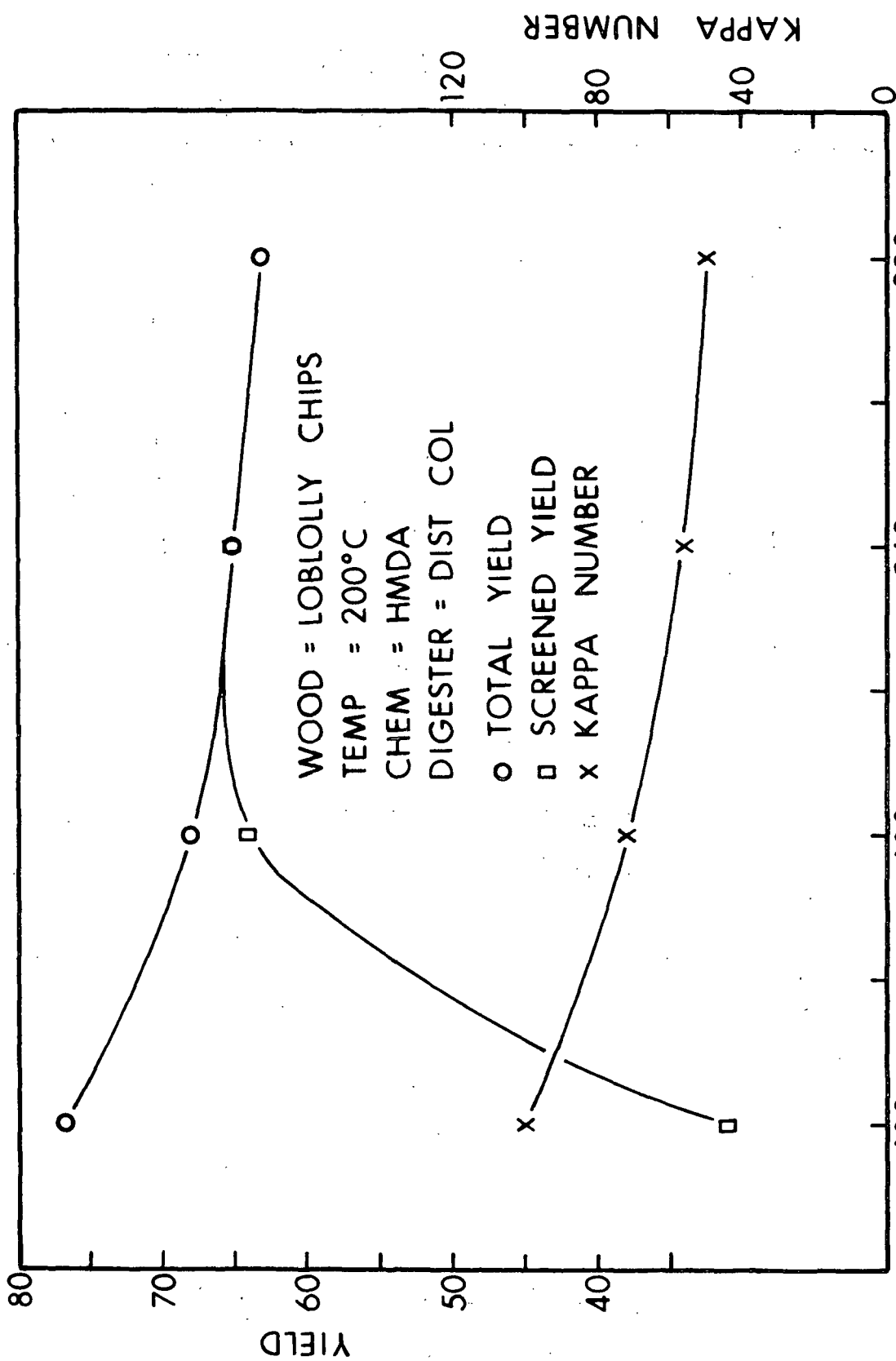

Figure 7. Yield and Kappa Number as a Function of Cooking Time for Loblolly in the Distillation Column Digester

For example, it has been observed that the lignin will precipitate from the black liquor upon addition to water. Thus fiberization of the chips and their subsequent washing in water will cause some of the lignin to precipitate on the fiber instead of being removed. In addition, the lignin itself is fluid above temperatures near 150°C and becomes a viscous material at room temperature. Consequently, the washing temperatures will also cause the lignin to become viscous and adhere to the fibers during the fiberization and washing processes, which contributes to the varying kappa numbers. These facts lend credence to the concept of separating the individual fibers and extracting the lignin from the fiber in fresh hot HMDA before coming into contact with water.

Examination of the pulping results shown in Fig. 8, where total yield is plotted versus the kappa number for aspen and loblolly pulps, leads to the same conclusion as expressed earlier, i.e., a constant yield can be obtained for the aspen pulps. Further chemical testing of the pulps (the results are tabulated in Tables II and III for aspen and loblolly, respectively) revealed the reason for this observance of a constant yield. Notice that the hemicellulose and cellulose contents of the pulps at all the cooking times correspond, within the experimental error, to the theoretical limit of about 64% obtainable from the wood chips.

This leads to the premise that the HMDA removes only the lignin and that the cellulosic material is not significantly removed by the action of this pulping process. Consequently, studies using this system as a tool for such separations may shed some light on the age old question of bonding between lignin and cellulosic materials and should be pursued further.

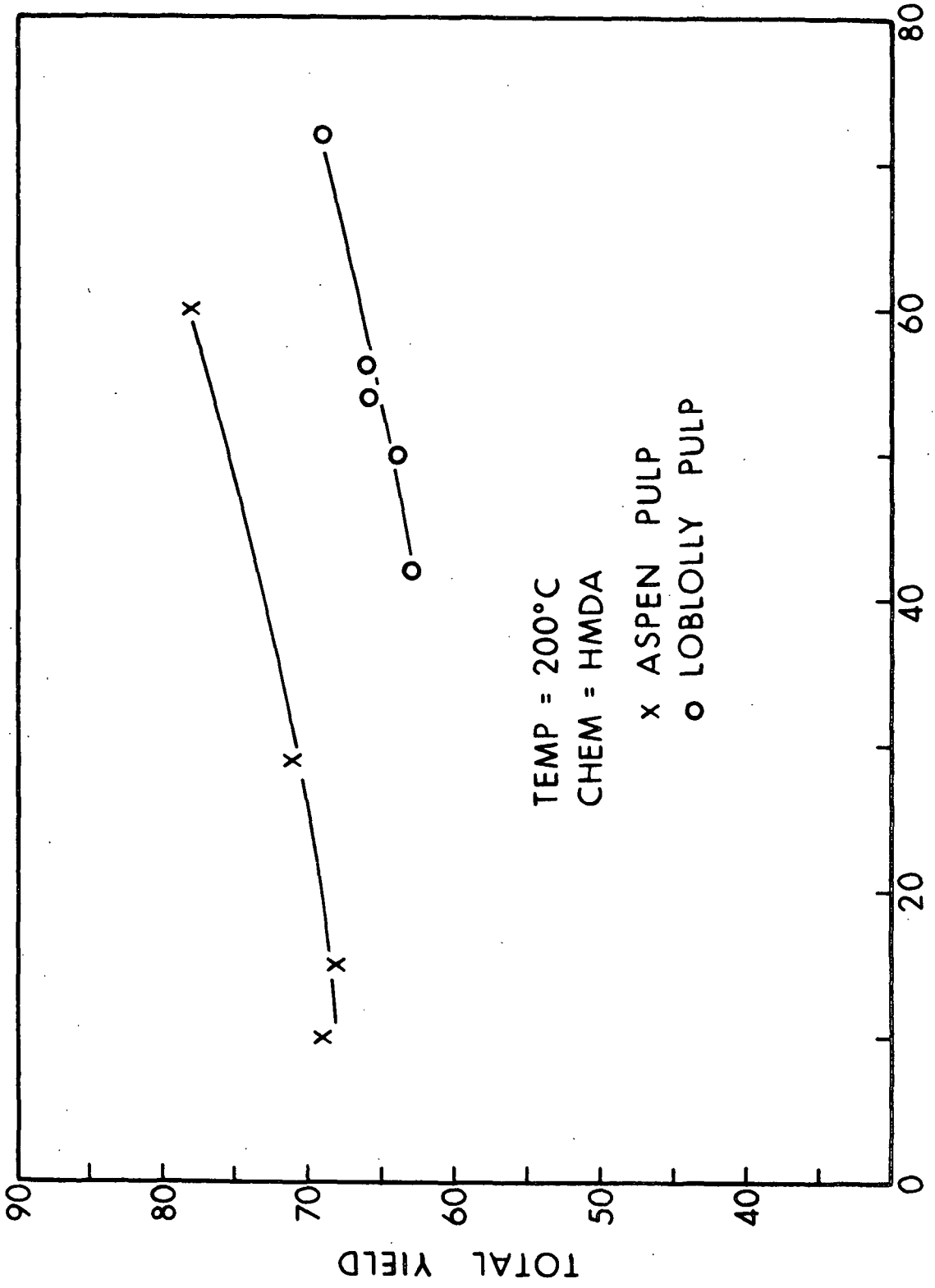

Figure 8. Yield-Kappa Number Relationship for Aspen and Loblolly

TABLE II

ASPEN PULPING AND TESTING RESULTS

Cook No.	105	101	108	107	Wood
Time, hr	1/2	1	2	4	-
Reject yield	11.7	-	-	-	
Accept yield	66.1	71.2	68.2	68.8	
Total yield	77.8	71.2	68.2	68.8	
Kappa No.	58.9	29.2	15.4	10.3	
*Klason lignin	5.8	2.1	0.4	0.3	17.8
*Soluble lignin	1.6	1.1	0.8	0.6	4.7
Holo yield	89.9	92.2	97.7	98.6	
Cuene vis. (cp)	50.4	41.0	30.0	21.4	
*Alc. - benzene extract	0.5	0.1	0.1	0.1	2.4
*Araban	0.4	0.3	0.1	0.1	0.4
*Xylan	15.2	14.4	14.8	15.7	16.3
*Mannan	1.8	1.7	1.4	1.5	2.0
*Galactan	0.6	0.5	0.3	0.3	0.8
*Glucan	46.1	44.8	44.3	46.0	44.1
Total Sugars	64.1	61.7	60.9	63.6	63.6

*Values are based on wood.

TABLE III

LOBLOLLY PULPING AND TESTING RESULTS

Cook No.	200	202	203	201	Wood
Time, hr	2	3	4	5	-
Reject yield	44.8	3.7	-		
Accept yield	32.5	65.1	66.1	64.0	
Total yield	77.2	68.8	66.1	64.0	
Kappa No.	100.8	71.5	55.9	49.0	
*Klason lignin	15.3	6.6	4.4	3.9	28.3
*Soluble lignin	0.6	0.6	0.5	0.5	0.3
Holo yield	84.1	90.2	94.1	94.2	
Cuene vis. (cp)	29.4	21.6	17.1	20.1	
*Alc. - benzene extract	0.2	0.3	0.1	0.2	1.6
*Araban	0.8	0.8	0.7	0.7	1.2
*Xylan	6.2	6.1	5.9	6.1	6.7
*Mannan	10.9	10.3	10.2	10.2	11.0
*Galactan	2.1	1.6	1.3	1.2	2.7
*Glucan	40.8	40.1	40.8	41.7	41.9
Total Sugars	60.8	58.9	58.9	59.9	63.5

*Values are based on wood.

The results for the loblolly generally substantiate the conclusions drawn from the aspen pulps. Although an extension of the data in Fig. 8 to lower kappa numbers would pin down the limiting yield value with more certainty, it appears that a yield around 60% is a limiting yield value. This is substantiated by the data in Table III.

BLEACHING RESULTS WITH CHLORINE AND CHLORINE DIOXIDE

The next series of chemical treatments are those using chlorine, sodium hydroxide and chlorine dioxide, commonly used in many bleaching processes. Two bleaching sequences, CEDED and CECECED were used on aspen and one CECECED was used on loblolly. The many stages were due to the fact that the pulps had higher initial lignin contents than are desirable and the bleaching stages were repeated until permanganate numbers below 4, preferably 1 or 2, were obtained.

The conditions and results of the treatment are contained in Tables IV, V, and VI. The D treatments with brackets [ ] represent small samples that were treated in order to determine the final amount of chlorine dioxide to use in order to obtain maximum brightness values. The brackets containing A or B were additional treatments and will be discussed later.

There are several points of interest. First, if the pulp losses occurring during the bleaching are attributed to the removal of only lignin, the relationship between lignin and kappa number is 0.17% yield/kappa number for aspen and is 0.14% yield/kappa number for loblolly. Within experimental error these are near the values for equivalent kraft pulps. In addition, the chlorine demand, i.e., the ratio of the weight percent of Cl_2 used to the kappa number, is 0.35 for aspen and 0.38 for the loblolly. This is close to the 0.38 expected for kraft pulps with the same kappa numbers.

TABLE IV

MULTISTAGE BLEACHING DATA FOR ASPEN

Stage	C	E	D	E	D(1)	D(2)	D(3)	D(4)	D	P	H
H_2O_2, %										1.0	
Sodium hypochlorite, %											1.0
Cl_2, %	5.0										
ClO_2, %			1.2		0.3	0.5	0.7	1.0	1.0		
Sodium hydroxide, %		2.75		1.25							.25
Consistency, %	3.0	10.0	10.0	10	10	10	10	10	10	10	10
Reaction temperature, °C	25	60	60	60	60	60	60	60	60	70	45
Reaction time, min	60	60	70	60	35	150	240	240	240	210	60
Final pH		11.0	2.5	11.3							11.2
Residual chemical, % applied	2.6		no		no	no	trace	yes	9.9	8.8	0
TAPPI brightness					64.8	69.9	72.8	73.2	73.0	83.2	80.9
Aged brightness									66.4	80.4	77.9
Bleached yield, %									92.1		
Permanganate number		10.8									
Na-Silicate 40-42°B, %										2.0	

The original aspen pulp had a yield of 68.2% with a kappa number of 29.8. The final pulp yield = 0.921 x 68.2 = 62.8%. The chlorine demand = 4.9 + (1.2 + 0.9) 2.62 = 10.4% on the pulp. The chlorine demand to kappa number ratio is 10.4 ÷ 29.8 = 0.35 wt.%/K no.

TABLE V

MULTISTAGE BLEACHING DATA FOR ASPEN

Stage	C	E	C	E	D(1)	C	E	D(2)	D(3)	D(4)	D	P	H
H_2O_2, %												1.0	
Sodium hypochlorite, %													1.0
Cl_2, %	4		3			2.0							
ClO_2,%					1.0			0.4	0.7	1.0	0.7		
Sodium hydroxide, %		2.75		1.25			1.0						0.25
Consistency, %	3	10	3	10	10	3	10	10	10	10	10	10	10
Reaction temperature, °C	25	60	25	60	60	25	60	60	60	60	60	70	45
Reaction time, min	55	60	60	60	90	60	60				240	210	55
Final pH		11.3		10.4			9.8				2.7	7.8	11.3
Residual chemical, % applied			3.2			4.8					6.4	18.5	0
TAPPI brightness					56.1			65.9	70.6	70.6	69.3	81.7	80.0
Aged brightness											65.0	79.6	77.1
Bleached yield, %											92.7		
Permanganate number		12.9		6.6			2.55						
Na-Silicate 40-42°B, %												2.0	

Unbleached pulp yield = 68.2
Bleached pulp yield = 68.2 x 0.927 = 63.2

Chlorine demand = 4.0 + 2.9 + 1.9 + 0.66 (2.62) = 10.5
(original kappa number = 29.8)

Chlorine demand = 10.5/29.8 = 0.35 wt.%/K no.

TABLE VI

MULTISTAGE BLEACHING DATA FOR LOBLOLLY

Stage	C	E	C	E	C	E	D(1)	D(2)	D(3)	D	P(A)	H(B)
H_2O_2 %											1.0	
Sodium hypochlorite, %												1.0
Cl_2, %	10.5		4.0		4.0							
ClO_2,%							0.4	0.7	1.0	0.7		
Sodium hydroxide, %		4.5		2.0		1.5						0.25
Consistency, %	3	10	3	10	3	10	10	10	10	10	10	10
Reaction temperature, °C	25	60	25	60	25	60	60	60	60	60	70	45
Reaction time, min	60	60	60	60	60	60	210	210	210	240	210	100
Final pH		11.0		11.5		11.2				2.8	8.4	11.4
Residual chemical, % applied	7.4		25.8		54					28.2	20.4	0
TAPPI brightness							74.5	76.0	75.5	75.6	83.5	81.9
Aged brightness										70.0	79.9	77.6
Bleached yield, %										90.8		
Permanganate number		9.85		5.6		1.40						
Na-Silicate 40-42°B, %											2.0	

Unbleached pulp yield = 63.1
Bleached pulp yield = 63.9 x 0.908 = 57.3%

Chlorine demand = 9.7 + 3.0 + 1.8 + 0.5 (2.62) = 15.81
= 15.81/original kappa no. = 15.81/42 = 0.38 wt.%/K no.

Second, the G.E. brightness of C, E and D bleaching sequences seems to be limited between 70 and 80. Two factors are likely candidates as reasons for not obtaining higher values, i.e., HMDA and/or hemicellulose have harmful effects on brightness. The data that we have does not differentiate between the two and further work will need to be done to resolve this question. In any case, it appears that the pulps are not easily bleached to high brightness values with chlorine or chlorine dioxide.

PEROXIDE AND HYPOCHLORITE BLEACHING

The bleached pulps were further treated in order to increase the brightness values. Each bleached pulp was treated separately with hydrogen peroxide or sodium hypochlorite. The conditions and results are shown in Tables IV, V, and VI and are listed under columns P(A) and H(B), respectively. The peroxide treatment showed the most improvement with values of 83+. The sodium hypochlorite gave results between 80 and 82. The net result is that these pulps can reach brightness values in the 80's.

Consideration of all the pulping and bleaching results thus far leads to the conclusion that the optimum brightness should be attained by first removing the lignin with HMDA, at least down to permanganate numbers below 5.0, and then using a short bleaching sequence, ending with a peroxide treatment.

The presence of the high hemicellulose content in these pulps should be useful for further study of the effect of hemicelluloses on bleaching processes. For example, bleaching these pulps and comparing the results to those for pulps obtained after removal of the hemicelluloses from these pulps should give results that reflect the effects of the hemicelluloses on the bleaching processes better than testing the results obtained by the addition of hemicelluloses to pulps that

are already low in the hemicelluloses. In other words, the large contents of in situ hemicellulosic material should, at low lignin contents, allow one to zero in on the effects of these high contents on the bleaching processes.

PULP VISCOSITIES

The cuene viscosities of these pulps were measured and are shown plotted in Fig. 9. Note that the viscosities drop fairly quickly and level off at a value near 20 cp. If these viscosities are converted to DP's using the Hercules conversion tables, the values are higher than expected for pulps containing so much hemicellulosic material. This points out the need for obtaining molecular weight distributions using some other techniques and then relating these to the viscosities, i.e., standardizing the viscosity measurements.

Samples of abaca and cotton were also subjected to extraction in HMDA and their results are also included in Fig. 9. The main point to note is that the resulting viscosities are much lower than the pulp values. This difference is very likely related to the high hemicellulosic content of the pulp and further studies should provide information regarding the role of the hemicelluloses on depolymerization of cellulosic materials.

Again the unique character of these pulps should provide insight to the effect of hemicellulose on DP's by studying the molecular weight distribution before and after the removal of the hemicellulosic material.

X-RAY DIFFRACTION RESULTS

Additional information relating to the fiber properties was obtained from x-ray diffraction analyses. Figure 10 shows the diffraction pattern of an amine pulp as compared to various crystalline forms of cellulose. It appears that it is

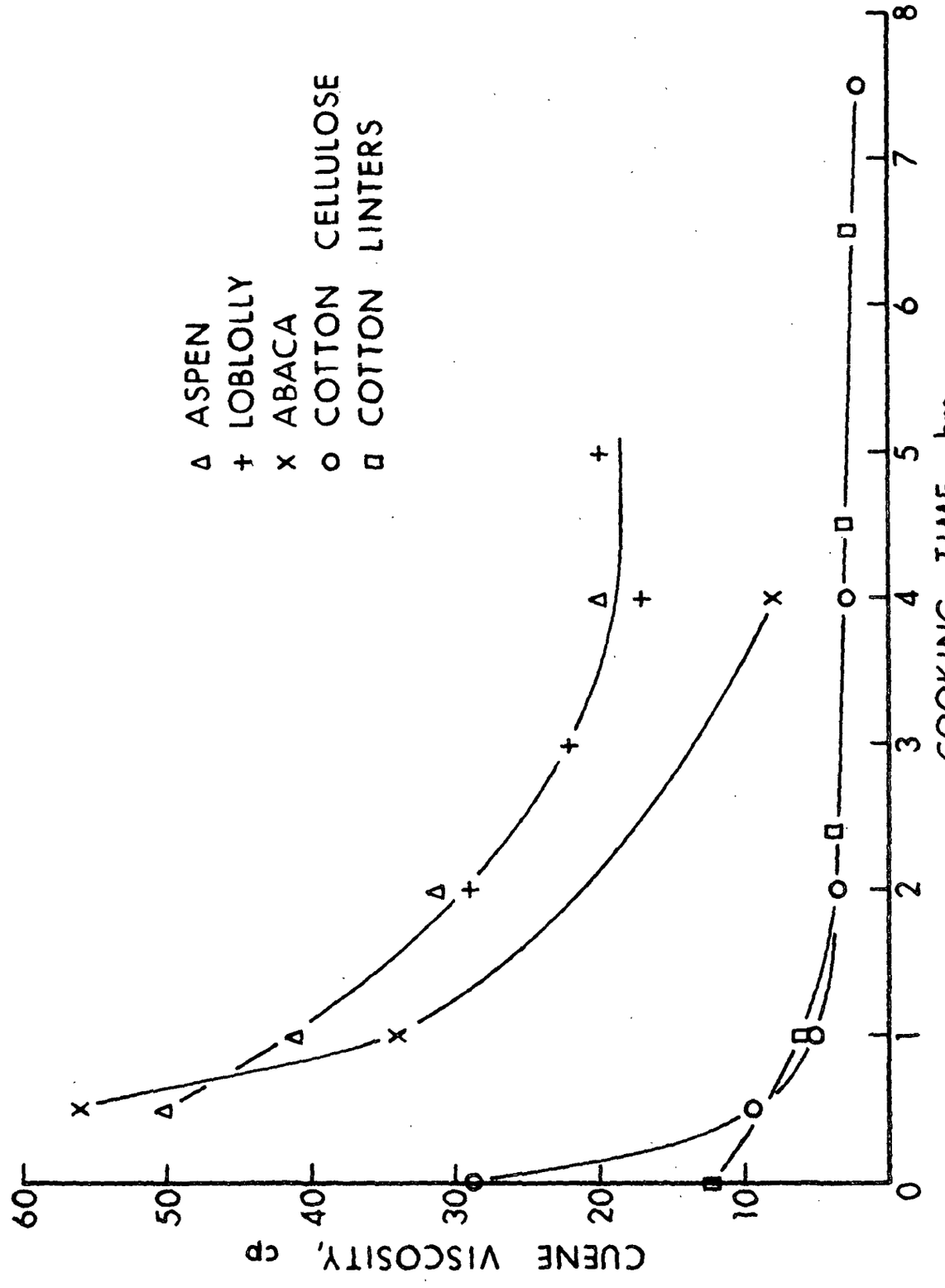

Figure 9. Viscosities of Pulps and Cellulosic Materials Treated in HMDA

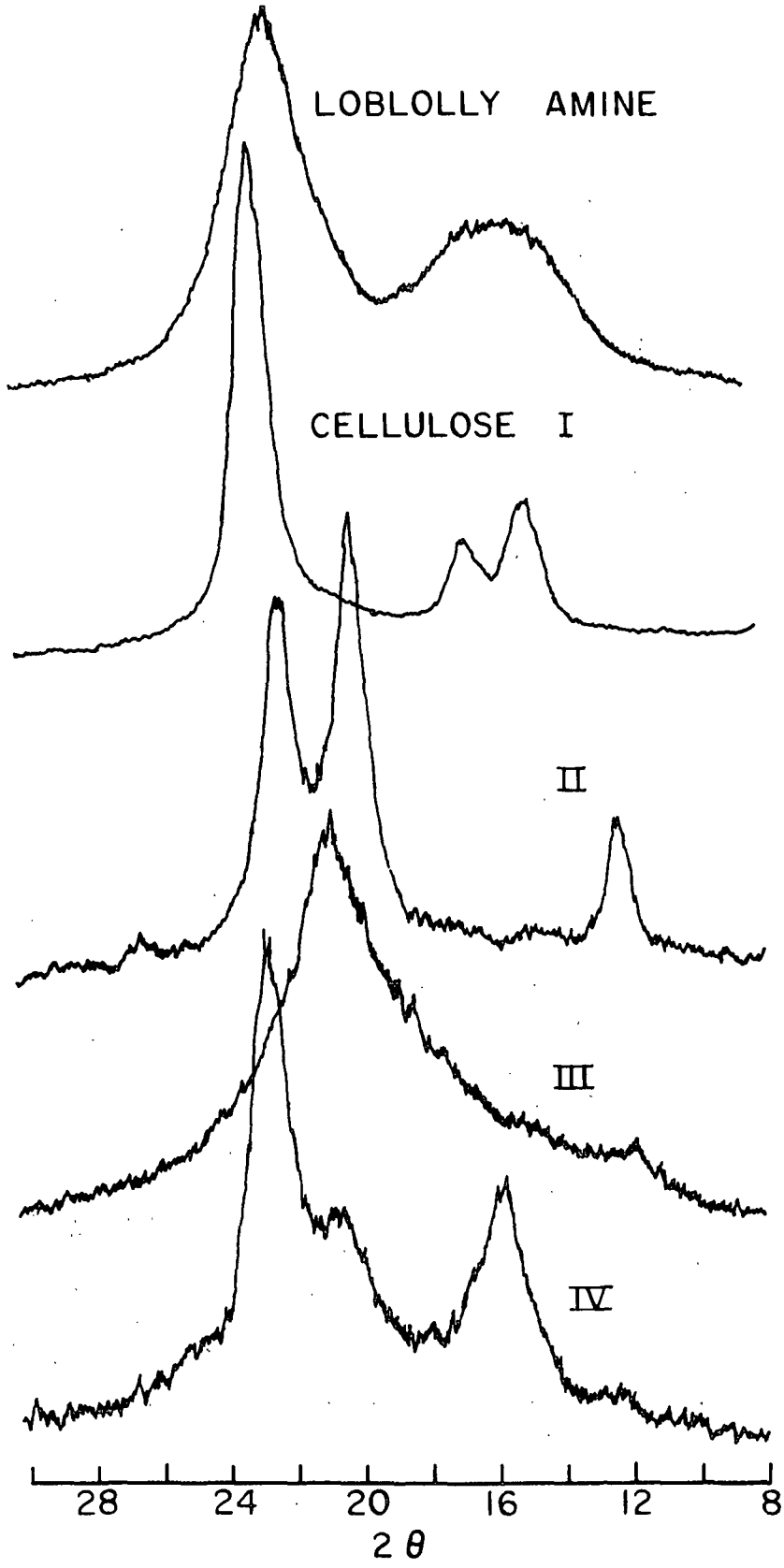

Figure 10. X-ray Pattern for Loblolly Pulp

either a noncrystalline form of cellulose I or a combination of celluloses I and IV. Further work using Raman spectra is anticipated but has not yet been accomplished.

The width at half-heights (whh) for the amine pulps are compared with those of some representative kraft pulps in Table VII. Note that the amine loblolly whh values are larger than those obtained for kraft and those of aspen are less than room temperature cellulose. These whh values are in the order of the relative handsheet strengths in the following way:

whh (loblolly) kraft < amine and strengths kraft > amine

whh (aspen) amine < holocelluloses and strengths amine > holocelluloses

Further work relating the crystallinity (represented by the whh values) to strengths might be illustrative of its role in fiber properties since it appears here that the stronger fibers are more crystalline, i.e., smaller whh values.

TABLE VII

X-RAY POWDER RESULTS ON PULP CRYSTALLINITY

	whh	Annealed whh	HMDA Cook - 205°C		
			Time, min	Yield, %	Kappa No.
Loblolly					
L 201	2.52	2.48	300	64	49.5
L 202	2.60	2.52	180	68.8	71.5
Kraft		2.32			
Aspen					
101	2.40	2.44	60	71.2	29.5
107	2.32	2.32	240	66.8	10.3
Room temp. holocellulose		2.52			

HANDSHEET PROPERTIES

Representative unbleached pulps were beaten and their properties compared to kraft pulps. These pulps were then bleached and beaten and compared to the unbleached pulps. Several interesting factors surfaced during this work and are discussed next.

ASPEN RESULTS

The first point of interest is shown in Fig. 11 where the freeness development for unbleached and bleached aspen is compared to unbleached kraft pulps. Note that all the aspen pulps retain a higher freeness during beating than does the kraft pulp. This will be an advantage if a faster drainage rate can be obtained at equivalent sheet strengths and thus allow higher speeds during the sheet forming process. For example if one compares the CSF at a given breaking length, i.e., 7.8 km from Fig. 17, we find the kraft pulp has a value of 380 ml and HMDA has a value of 440 ml, thus giving a faster drainage rate for the HMDA pulp. It is also an indication that the HMDA fibers are stronger than the kraft fibers.

Results of the strength factors are shown plotted versus density in Fig. 12, 13, and 14 for aspen. The zero span measurements show equivalent strengths for kraft and HMDA pulps depending upon the chosen densities. However, the HMDA handsheets undoubtedly contain fewer fibers than the kraft pulp and the relative strength per fiber is even stronger if these values are multiplied by their respective yields as a means to approximate the relative sizes of the fibers. In any case, both fibers are strong.

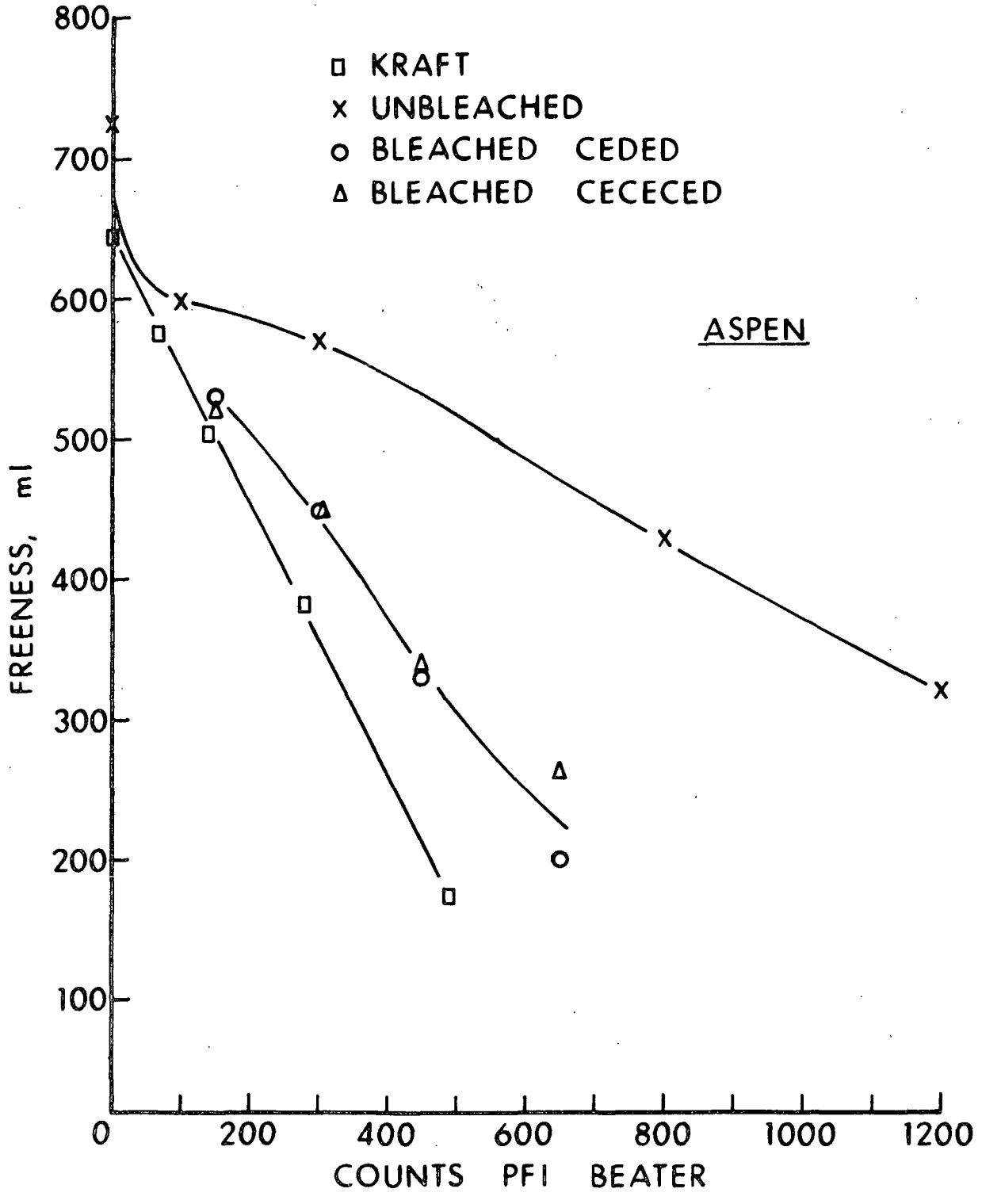

Figure 11. Freeness Development for Aspen in a PFI Mill

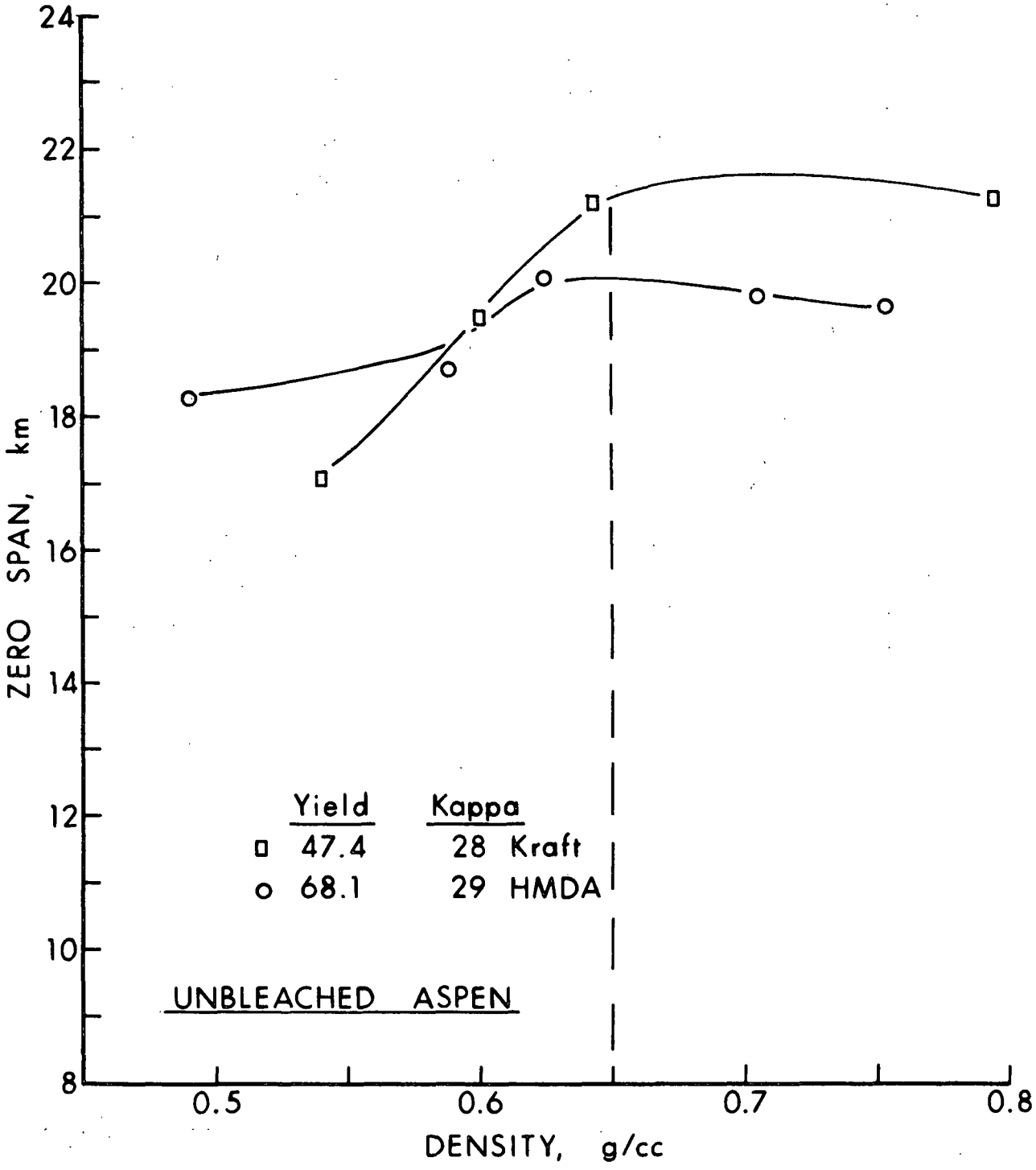

Figure 12. Zero-span Strengths as a Function of Density for Aspen

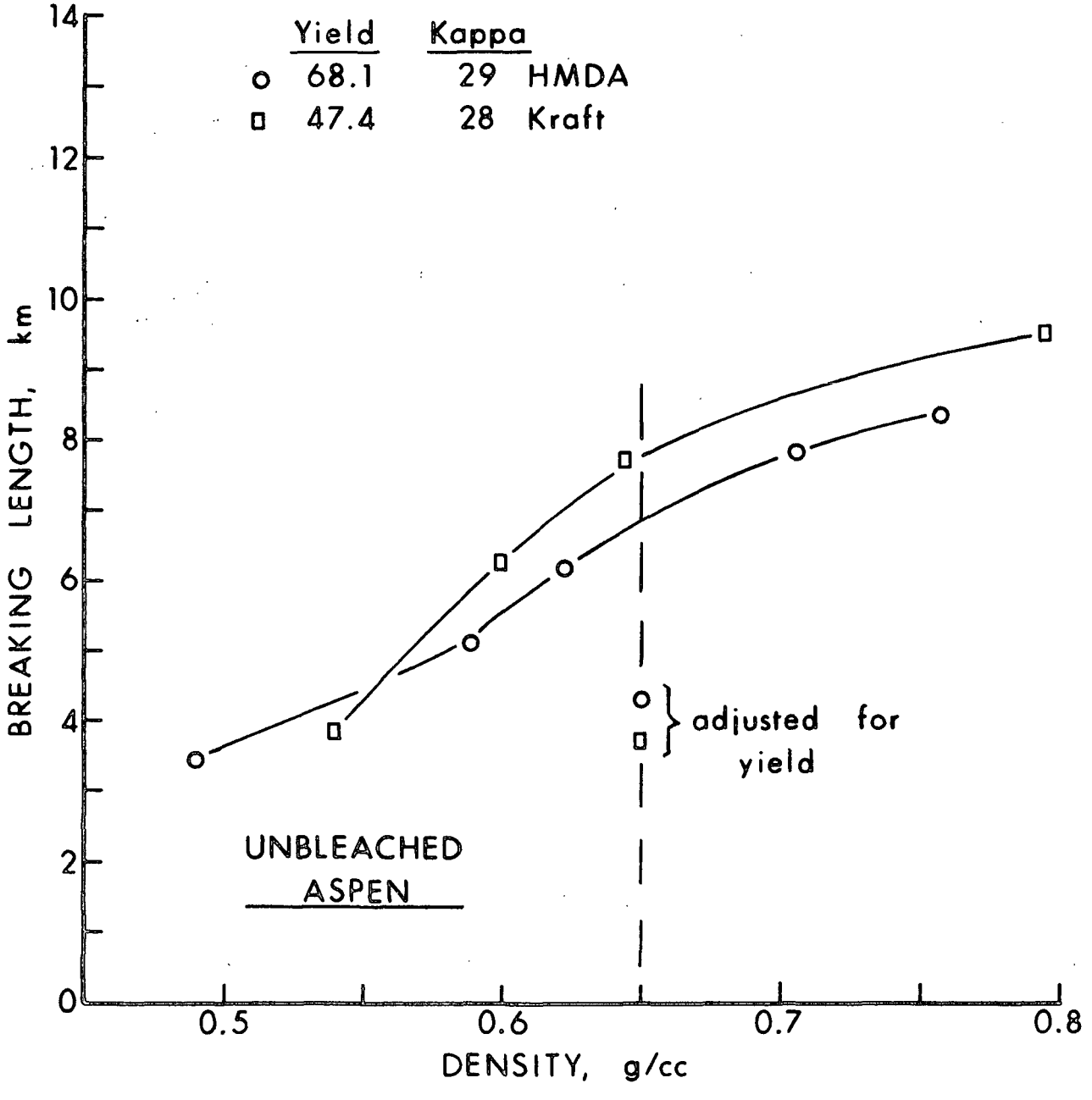

Figure 13. Breaking Lengths as a Function of Density for Aspen

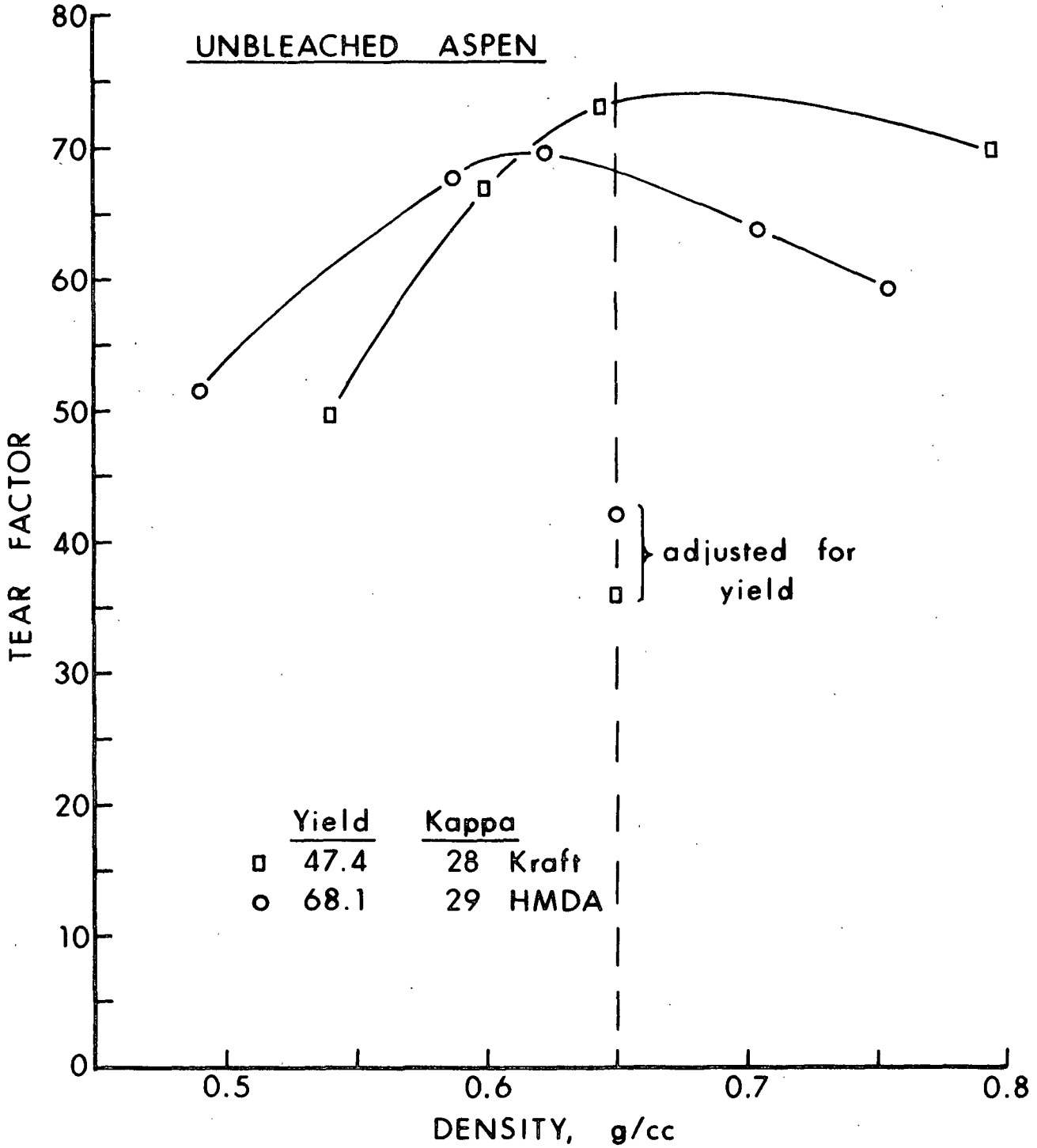

Figure 14. Tear Strengths as a Function of Density for Aspen

These results are evidence that the HMDA aspen fibers are strong and can form good handsheets. The breaking lengths and tear factors of both aspen pulps are very similar and at a given density their relative strengths may reverse orders. However, if one considers the process where a given strength is needed for a specific paper, the added yield obtained from the HMDA pulp will allow more paper produced from a given wood source. The relative values are shown on the plots as the points labelled "adjusted for yield."

LOBLOLLY RESULTS

The results for the unbleached loblolly are different in that the HMDA pulp beats up faster than the two kraft pulps and acts more nearly like a combination of the two (see Fig. 15). At the beginning it has freeness like the high lignin kraft pulp and at later times like the low lignin kraft pulp. The bleached HMDA pulp develops freeness much faster than all the others. This is evidence that the HMDA fibers are more fragile than the kraft fibers.

The results of the handsheet strength properties plotted versus densities for loblolly are shown in Fig. 16, 17, and 18. The zero span strengths at a given density are lower for the HMDA pulp than the kraft pulps and even if one adjusted these values by the relative yield factors the HMDA fibers have a lower zero-span value. This is an indication that HMDA loblolly fibers are weaker than the kraft fibers, although they may not be as much weaker as the unadjusted values would indicate.

The breaking length and tear factors for the HMDA handsheets are lower and even multiplication by the yield factors does not bring the values as high as the kraft pulps. This evidence indicates that the loblolly fibers are weaker than the kraft fibers or in any case do not form strong handsheets.

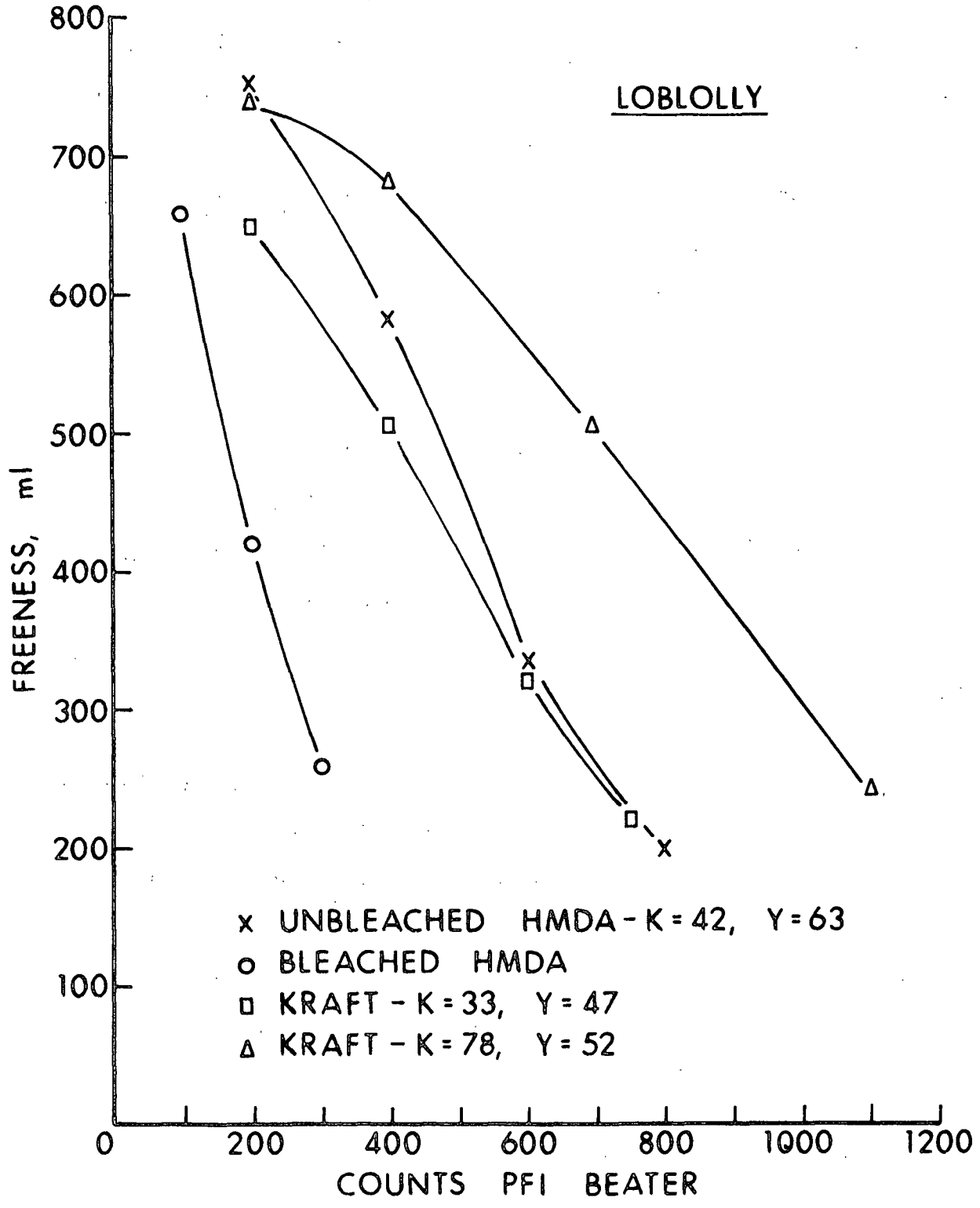

Figure 15. Freeness Development for Loblolly in a PFI Mill

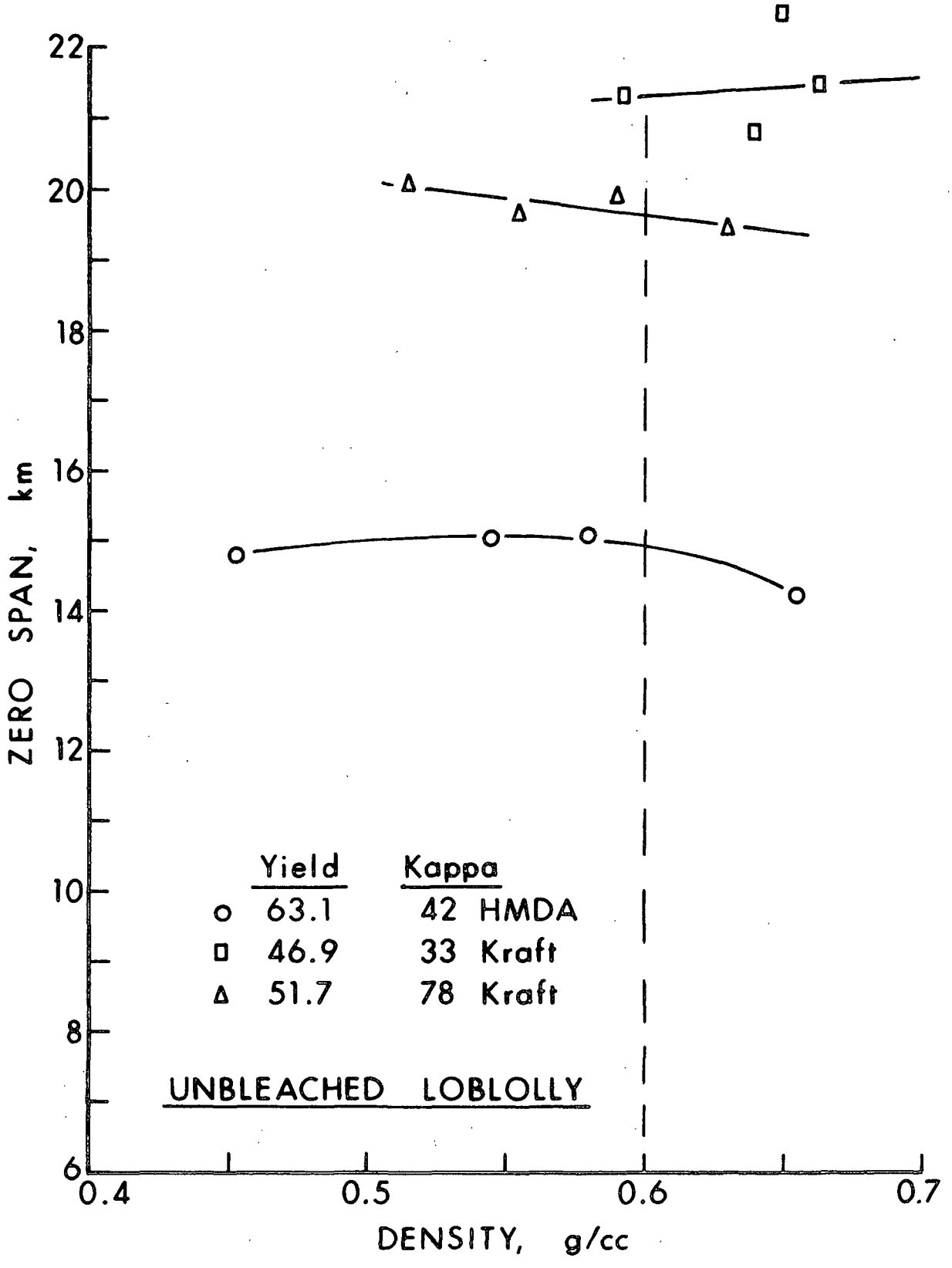

Figure 16. Zero-span Strengths as a Function of Density for Loblolly

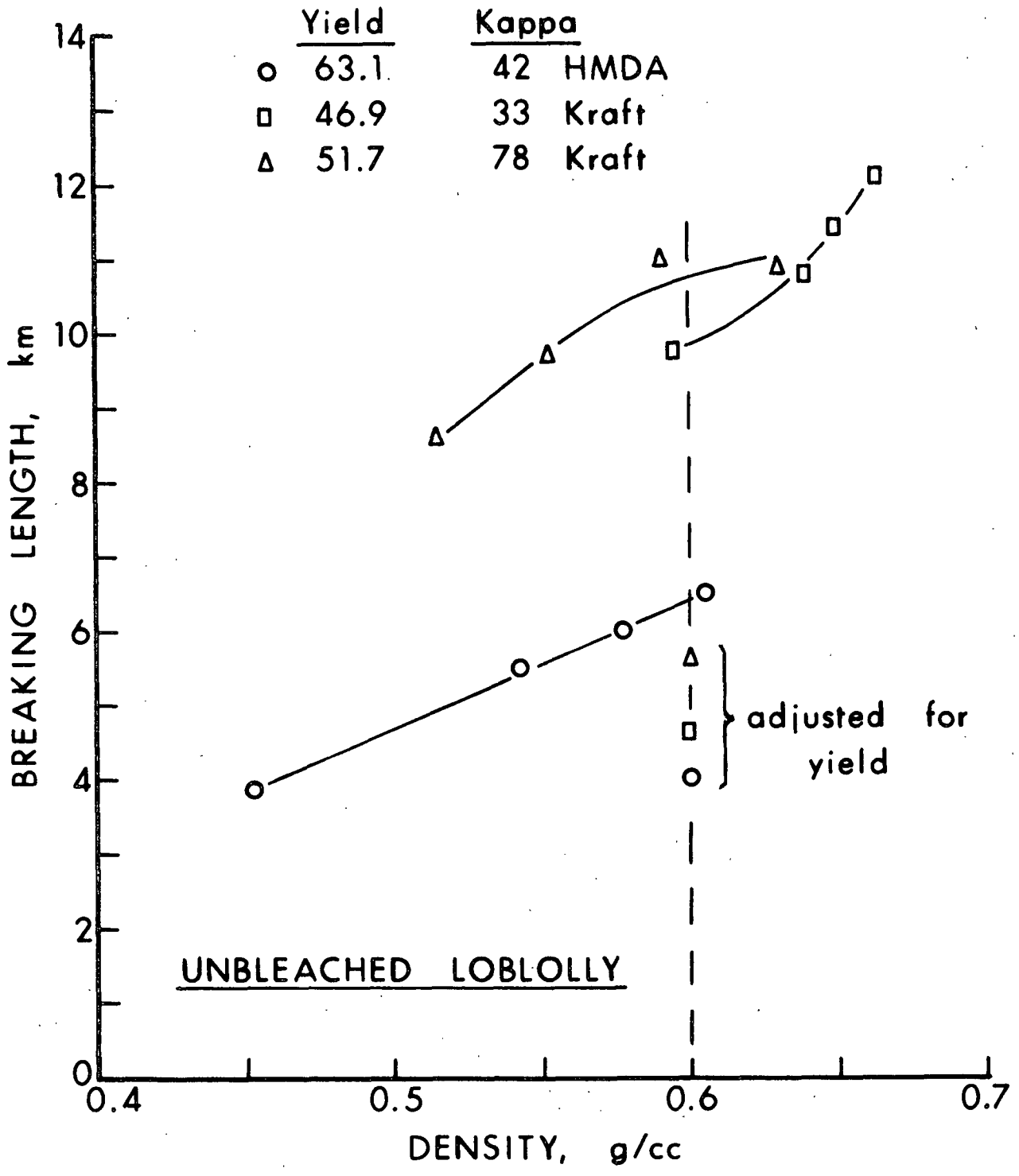

Figure 17. Breaking Lengths as a Function of Density for Loblolly

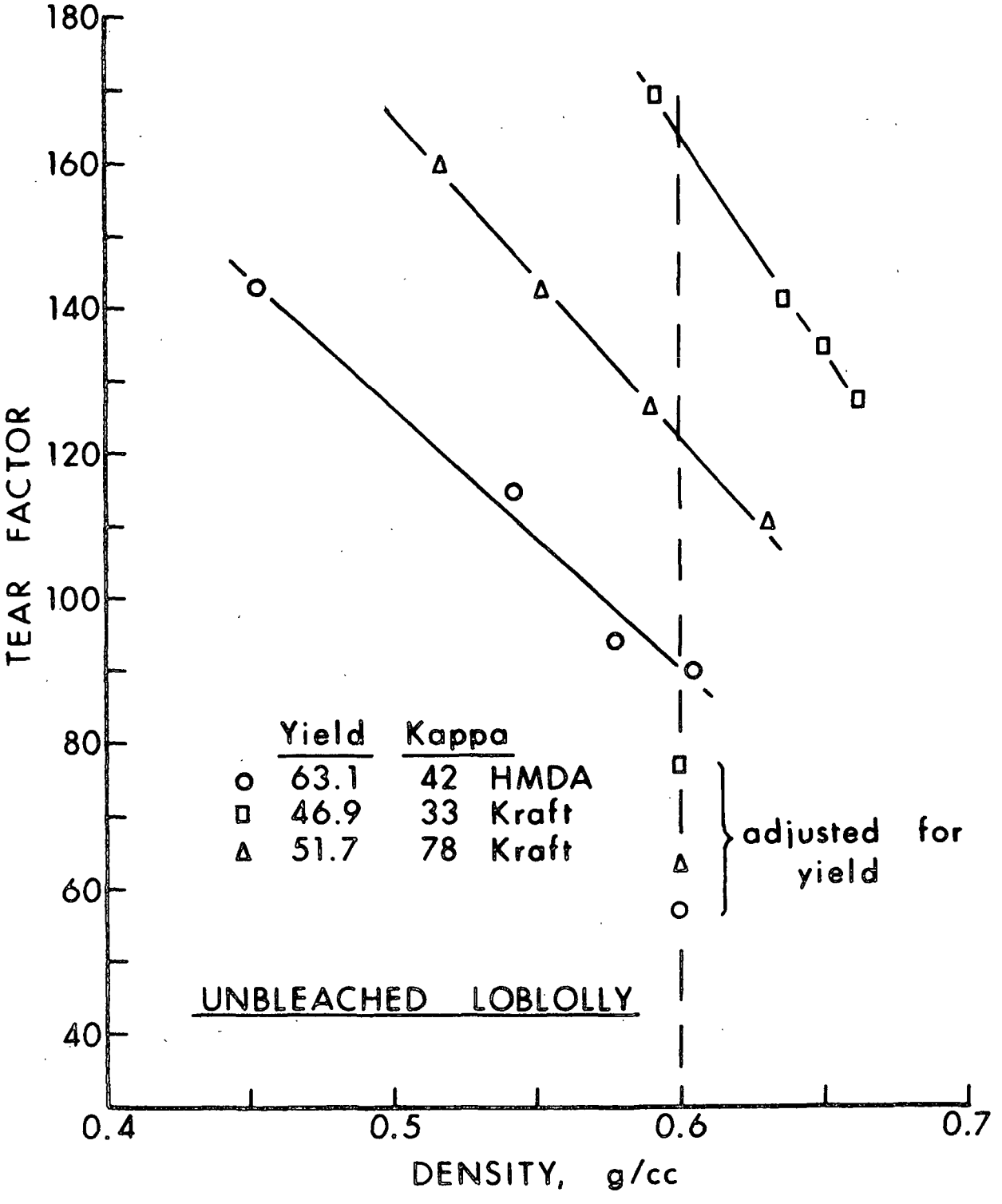

Figure 18. Tear Strengths as a Function of Density for Loblolly

BLEACHED HANDSHEET STRENGTHS

The bleached handsheet results for aspen and loblolly are shown in Fig. 19 and 20. There are two points of interest. For both species, the breaking lengths were virtually unchanged after bleaching when compared at a given density. The densities obtained from the bleached pulps were higher and the breaking lengths longer, but the plots show a simple extension of the curves obtained for the unbleached pulps. This is an indication that the bleaching processes do not degrade the fiber strengths.

The bleached tear factors, however, showed marked increases at a given density for both the aspen and loblolly pulps. These results demonstrate that the bleaching of the pulps is helping the interfiber bonding developed during the beating. Thus the fibers may be stronger than the unbleached handsheet properties have thus far indicated and the low values for the unbleached pulps may be due in part to poorer sheet formation when lignin is present rather than an inherent weakness in the fiber. There were no zero-span comparisons available for the bleached kraft pulps to make the comparison for fiber strengths.

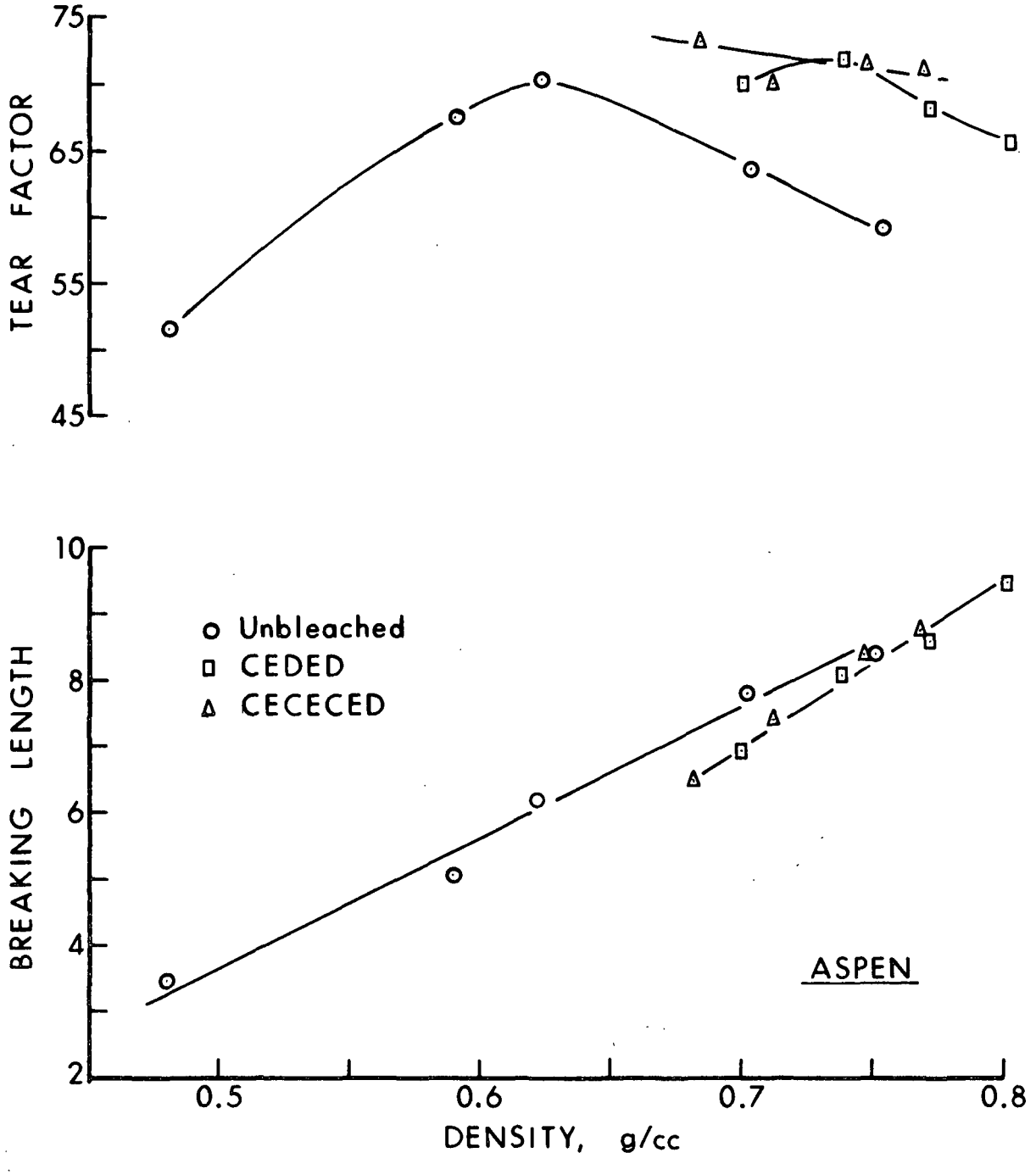

Figure 19. Breaking Lengths and Tear Factors for Bleached and Unbleached Aspen

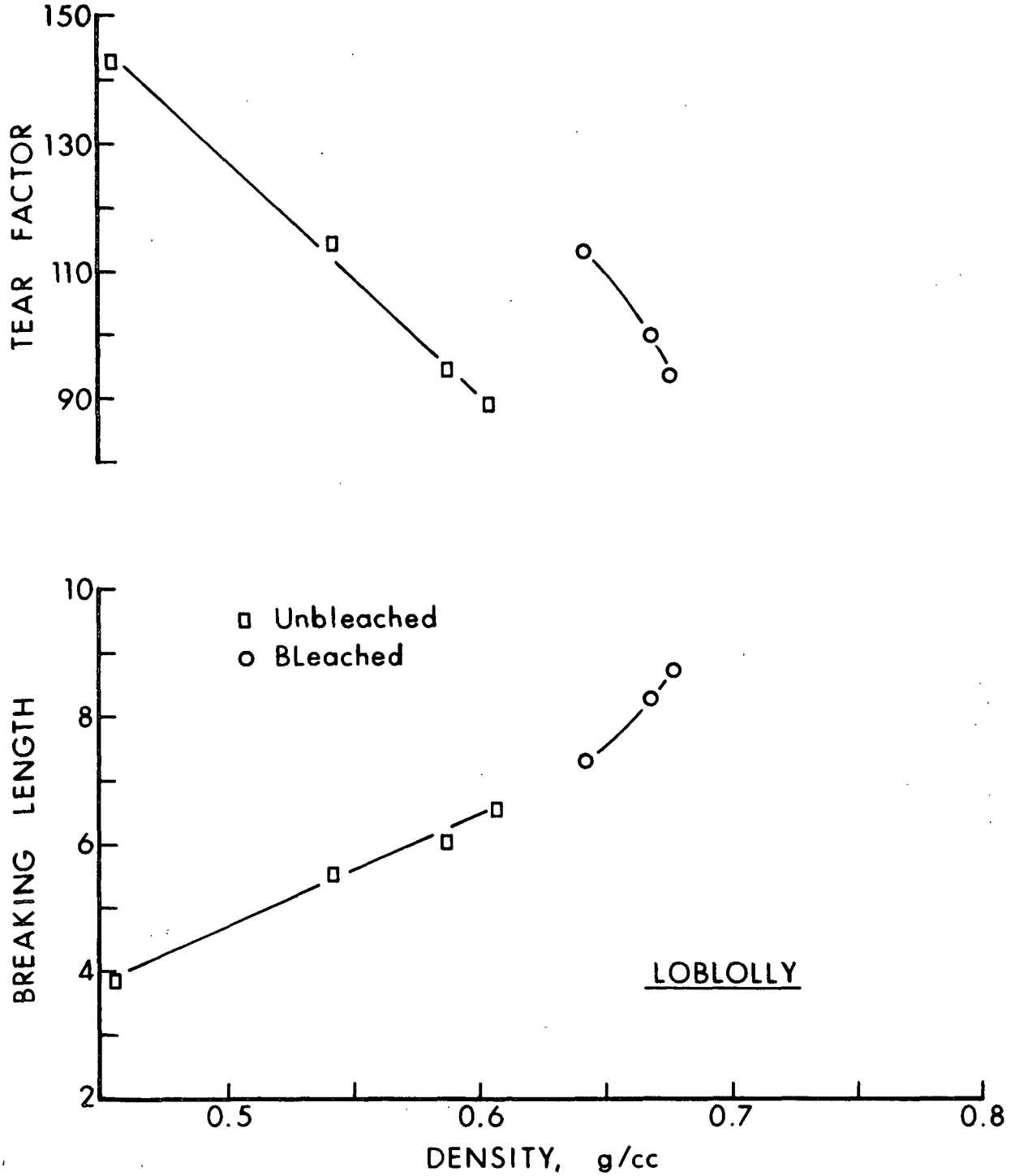

Figure 20. Breaking Length and Tear Factors for Bleached and Unbleached Loblolly

BLACK LIQUOR

Two modes of operation were used to examine the black liquor. The first consisted of removing lignin from the black liquor, and the second consisted of removing the HMDA from the black liquor.

LIGNIN REMOVAL FROM BLACK LIQUOR

Removal of the lignin from the black liquor can be accomplished by several means. First, dilution of the black liquor by water will cause the lignin to flocculate and then precipitate out of solution. Secondly, the lignin can be flocculated by adding an acid to the black liquor solution. A curious phenomenon occurs during this second procedure. That is, the lignin is soluble above a pH of approximately 11, insoluble between a pH of 11 and 8, and redissolves below a pH of 7. In fact, the lignin has remained soluble in pH's as low as 2 or 3. This is not characteristic of most lignins. Lignin can also be precipitated using divalent cations.

In all cases, once the lignin has been removed from solution and dried, either by freeze drying or heating in an oven, it is not very soluble in most solvents and dissolves slowly even in HMDA solutions. The infrared spectra of a lignin isolated by precipitation of lignin with HCl, a lignin isolated by evaporating the HMDA at high temperatures (up to 400°C) and of HMDA are shown in Fig. 21.

There are several major points to be mentioned. First the intense band of HMDA at 1540 cm^{-1} is not prominent in either of the lignin spectra. Thus the spectra (I and II) are assumed to be characteristic of the lignin even though there is much overlapping of the HMDA bands with the lignin bands in some regions.

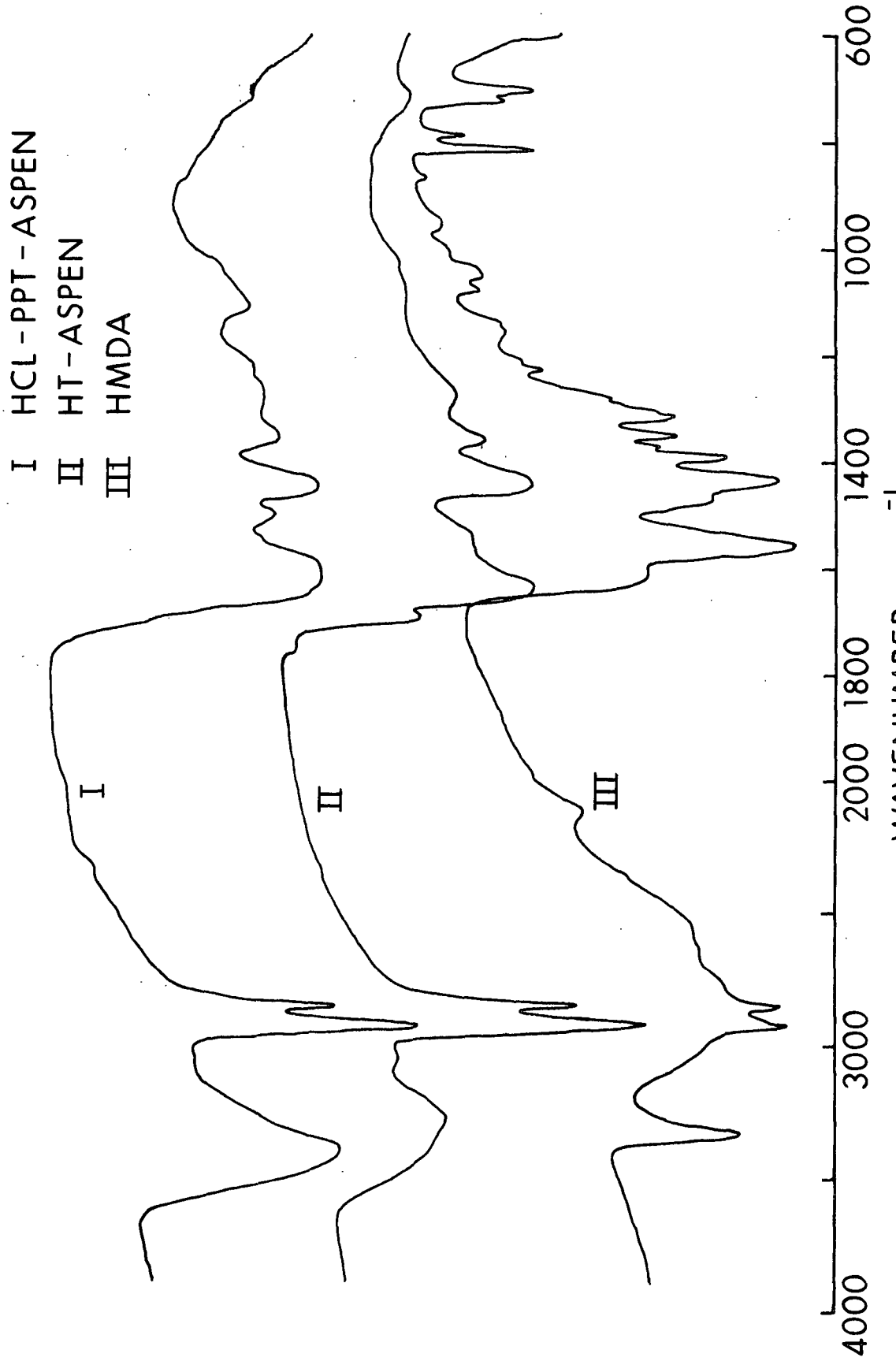

Figure 21. Infrared Spectra of Lignin

Next, the presence of an absorption band at 1700 cm^{-1} is an indication of a free $\rangle C = O$ moiety in the spectrum of the high temperature lignin. Note that this band is absent for the HCl-precipitated lignin. This can be interpreted as an indication that heating of the lignin has caused dissociation of a complex containing a $\rangle C = O$ functional group and some other entity. Examination of the 3400 cm^{-1} region, an area that is associated with hydrogen bonded functional groups such as -OH, shows that the high temperature lignin (II) has fewer such functional groups than the HCl-precipitated lignin (I) based on relative intensities. This is consistent with dissociation of a complex or removal of -OH functional groups.

These results are evidence that heating has caused separation of a complexed acidic functional group, i.e., $-\overset{O}{\overset{\|}{C}}-OH$, from its conjugated base. In addition the absence of $\rangle C = O$ absorption in the HCl-precipitated lignin can be attributed to formation of an acid-base complex. The net result of this evidence is that acidic lignin functional groups are likely to be associated with a base, in this case HMDA, and that heat can dissociate this complex.

HMDA REMOVAL FROM BLACK LIQUOR

The other mode of operation, the removal of HMDA from the black liquor by simply boiling the black liquor under atmospheric pressure was examined. The material in the pot usually boiled at 210°C at the beginning and was raised to nearly 400°C in most cases. At all times there were some vapors condensing and the reaction was stopped because of the limitations of the apparatus. For both aspen and loblolly, some sort of transition occurred between 290 and 310°C, in which gases were evolved causing foaming of the liquor. Once this action had ceased, continued heating caused further evaporation, and it appeared that the liquor could be taken to even higher temperatures.

The nitrogen analyses of the residues obtained in this way showed the amine contents could be around 30% by weight. Removing the amine from the lignin in a flask in this manner has several disadvantages. The first is that only a limited surface area is available for evaporation causing physical entrapment of the amine in the liquor, and the second was that the process is carried out at atmospheric pressure, causing the boiling temperatures to be high and possibly resulting in further chemical reactions. These can be overcome using appropriate equipment and would probably lead to a higher recovery of the amine without having heating effects on the lignin. This is a point for further work.

HYDROGENATION OF BLACK LIQUOR LIGNIN

The residue from this evaporation was further treated by a hydrogenation process. The conditions and results are shown in Table VIII. Examination of the liquid organic materials was carried out using ^{1}H and ^{13}C magnetic resonance spectra and a gas chromatographic separation and analysis.

The ^{13}C spectra shown in Fig. 22 substantiated these results and revealed that the major components are $-CH_3$ carbons and two different kinds of $-CH_2$ carbons. This evidence is used to conclude that the hydrogenation products are aliphatic hydrocarbons and do not contain any oxygen functional groups.

The ^{1}H magnetic resonance spectra (see Fig. 23) revealed hydrogen atoms associated with saturated hydrocarbons to be the predominant species. These are the peaks at shifts below 2.0 ppm. The peaks associated with aromatic nuclei are found shifted past 7.0 ppm and are much less intense than the others. In addition there is little evidence of hydroxyl hydrogens that would be between these two areas.

TABLE VIII

HYDROGENATION OF LIQUOR

Rxn. Conditions

75.0 g Lignin (ground); 37.5 g Harshaw HT-500-E 1/16 (presulfided); 1775 psi initial H_2 (∿ 10g)

450°C; 2 hrs. at temp.; 1:30 heat up time; 1:25 cool down time to 150°C; 1 liter autoclave with magnetic stirrer (Autoclave Engineers, Inc.)

Gases collected at 150°C through one 0°C trap and two -78°C trap.

Data

Total recovery 92%; 7.1 g water, 27.7 g organic liquids from cold traps, 25.0 g gases, 52.9 g remaining in autoclave after gases removed

Gases: 1775 psi initial, ∿ 3600 psi max., 3200 psi final; 60.8 ℓ gas recovered, 0.411 g/ℓ, strong NH_3 odor

Product remaining in autoclave: 52.9 g of which 37.5 g is catalyst and 15.4 g organics; consistency of dry powder; this product is normally distilled but the consistency did not allow it.

Lignin	75.0 g	100 %
H_2O	7.1 g	9.5 %
Liquid organics	27.7 g	36.3 %
Organics remaining in autoclave	15.4 g	20.5 %
Gas	∿ 15 g	20 %
Unaccounted	9.3 g	12.4 %

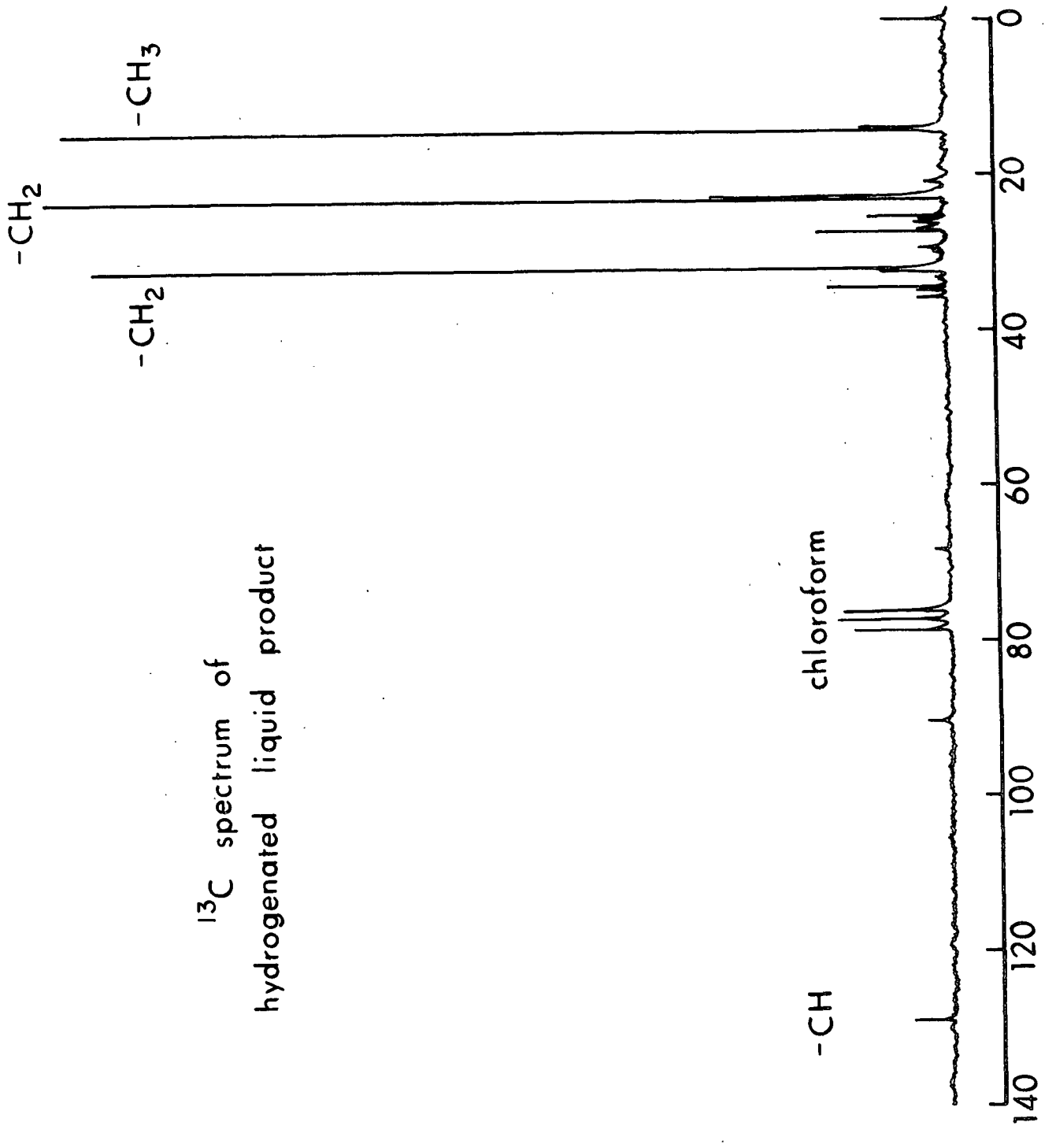

Figure 22. ^{13}C Magnetic Resonance Spectra of Hydrogenated Lignin Product

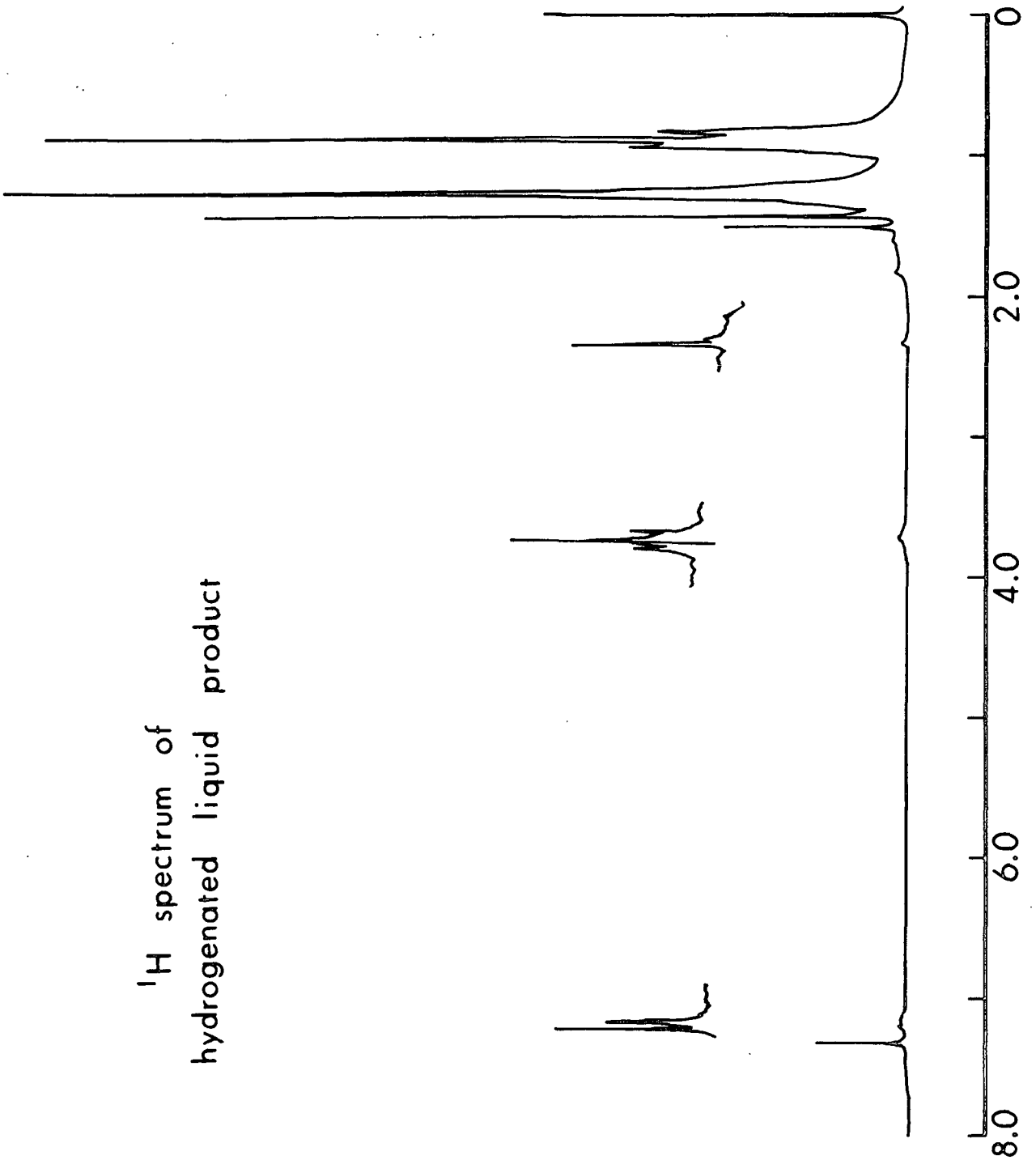

Figure 23. ^{1}H Magnetic Resonance Spectra of Hydrogenated Lignin Product

A gas chromatographic separation was then carried out and the results are tabulated in Table IX. Note that a majority of the hydrocarbons caught in the -78°C trap have the same retention times as the samples listed. The organic liquid collected at 0°C has many of the same retention times as the samples tried, but there are many more peaks at longer times and can be attributed to higher molecular weight compounds.

If one assumes that the gases collected are also saturated hydrocarbons the total sample produces a total of 56.8% (inclusion of the 12.4% unaccounted would give 69.2%) conversion of the black liquor residues to saturated hydrocarbons. If the nitrogen contained in this sample were all HMDA, about 30% of the sample would be amine. Thus at least 26.8 to 39.2% of the total sample, or (26.8/70 to 39.2/70) 38 to 56% of the lignin, was converted to aliphatic hydrocarbons.

This evidence leads to the conclusion that the hydrogenation of the black liquor residue has caused cleavage of the polymeric lignin, saturation of the aromatic nuclei and removal of oxygen from the lignin samples.

These results show the need for further study on the hydrogenation products, both from the viewpoint of deducing information about the structure of lignin and the utilization of the black liquor from this process as a feed stock for producing chemicals.

TABLE IX

CHROMATOGRAPHIC IDENTIFICATION OF LIQUIDS
FROM HYDROGENATED BLACK LIQUOR

-78°C			°C	
Time	Relative Intensity	Identity	Time	Relative Intensity
3.48	5.2		3.95	2.4
3.91	15.6	Pentane	4.77	27.8
4.71	51.8	Hexane	5.55	1.5
5.47	2.6	Cyclopentane	6.28	7.1
6.25	6.6	Heptane	7.50	4.7
7.48	5.2	Cyclohexane	8.88	11.4
8.87	4.3		12.96	3.2
	91.3		13.81	2.6
			18.49	2.6
			25.12	3.9
			32.25	2.2
			35.21	2.0
				71.4

ECONOMIC FACTORS

An economic analysis was not carried out, but the major factors to consider are as follows. First, the solvent is costly, approximately $1.00/lb and any process will be sensitive to accidental losses. On the brighter side, the fact that pulping can be done under atmospheric pressure is likely to lead to less expensive digester equipment.

The properties of the high yield pulps in terms of hemicellulosic material, slow beating and low densities offers possibilities for new uses of the pulp. In addition, the lignin isolated in this process is freer of cellulosic material and its potential as a chemical feedstock holds much promise. In any case more work needs to be done to characterize such uses and form a basis for a sound economical evaluation.

CONCLUSIONS

The experimental work accomplished here has formed a basis for the pulp properties of bleached and unbleached aspen and loblolly pine, characterized their handsheet properties, examined pulping procedures and touched upon the treatment of the black liquor for a HMDA pulping system.

It has been found that pulp yields higher than those from kraft processes are obtainable at equivalent or lower lignin contents. The HMDA aspen pulps have been found to be as strong or stronger than the kraft aspen pulps whereas the HMDA loblolly pulps are weaker. Both pulps have been found difficult to bleach to high brightnesses with chlorine, caustic and chlorine dioxide treatments.

In order to provide a sound basis for a future economic evaluation, the goals have been extended to include the following:

1. Obtain pulp with minimum lignin content using only amine pulping agent,
2. characterize the lignin removed from the wood and examine the removal mechanism, and
3. study the potential of the black liquor as a chemical feed stock.

These activities will be carried on by the author at Michigan Tech. Cooporation with the IPC staff will continue on an informal basis.

THE INSTITUTE OF PAPER CHEMISTRY

Larry M. Julien

Larry M. Julien
Visiting Research Associate
Delignification Division

Reviewed by

E W Malcolm

Earl W. Malcolm
Director
Chemical Sciences Division